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STORS: The Sludge-to-Oil Reactor System

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STORS: THE SLUDGE-TO-OIL REACTOR SYSTEM

by

P.M. Molton, A.G. Fassbender, and M.D. Brown
Battelle-Northwest
Richland, Washington 99352

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Project Officer

Howard Wall
Wastewater Research Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

The Sludge-to-Oil Reactor System (STORS) continuously converted over 400 gallons (20 percent solids) of sewage sludge to oil during 100 hours of operation. About 80 percent of the energy in the sludge was recovered as an oil and char. The energy recovered was sufficient to make the STORS energy self-sufficient assuming the char is burned to furnish the heat for the process. STORS, when fully developed, appears to be another option competitive with incineration for sludge disposal. One test performed by spiking the sludge with pesticides indicated that some of the pesticides were totally destroyed and others were partly destroyed during processing.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major Congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The report describes the development of a continuous process that will convert municipal wastewater primary sludge into a useful nonpolluting product having properties similar to No. 6 fuel oil and usable as boiler fuel. The product is also a projection of a method that can be used to recover energy from wastes and save fossil fuels. This work is one of the tools necessary to assess how the ultimate disposal of municipal wastewater sludge can be done in a manner that will make it a truly valuable and profitable resource.

Francis T. Mayo, Director
Water Engineering Research
Laboratory

ABSTRACT

Direct, continuous thermochemical liquefaction of primary undigested municipal sewage sludge was carried out to produce a heavy oil and char product suitable for use as a boiler fuel. The process was highly energy-efficient in that up to 73% of the energy content of the 20% solids feedstock was recovered as combustible products (oil and char) that were essentially dry. The oil product had a heating value of 80% to 90% that of diesel fuel. These products are capable of supplying the energy requirements for dewatering and liquefaction. Thus a wastewater treatment plant based on the liquefaction concept can, in principle, be energy-self-sufficient.

Wastewater from the process was highly biodegradable, based on a standard BOD determination. The only other byproduct was a gas that is characteristically more than 95% carbon dioxide. The process is therefore relatively nonpolluting.

The prototype continuous liquefaction reactor was operated for more than 100 hours without any sign of corrosion or char buildup on the inside walls. Complete feedstock conversion was achieved at 300°C with a nominal 1.5-hr. residence time, or 5.8 kg/hr of solids throughput. An economic assessment prepared for a conceptual commercial liquefaction reactor indicated a cost of $45/dry tonne, which is highly competitive with incineration. Projected capital construction costs for a liquefaction unit, however, were $6.1 million, which is much lower than that for an incineration plant. The process therefore has considerable promise for many potential sites in the United States at the present time.

This report was submitted in fulfillment of Contract No. 810690-01-0 by Battelle-Northwest under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1983 to June 1985, and work was completed as of June 30, 1985.

CONTENTS

Foreword iii
Abstract iv
Figures vii
Tables viii
1. Introduction 1
2. Conclusions 2
3. Recommendations 3
4. Materials and Methods 4
    Reactor Design 4
    Sludge Feedstock Preparation 12
    Analytical Methods 12
    Sludge Analysis 14
        Oil Analysis 15
        Char Analysis 16
        Wastewater Analysis 17
5. Results and Discussion 19
    Reactor Testing 19
    Reactor Operating Experience 23
    Discussion of Reactor Operation 26
    Sludge Composition 28
    Oil Characterization 32
    Char Characterization 39
    Product Yields and Reaction Conditions 43
    Data Reduction 44
    Liquefaction Chemistry 48
    Gas Analysis 51
    Wastewater Characterization 53
6. Liquefaction Process Preliminary Economics 56
    Introduction 56
    Estimate Basis 56
    Cost Estimate Summary 60
7. Overall Achievement of Project Objectives 65

References 67

Appendix A: Reactor temperature and pressure profiles, runs 208-509 . 68
Appendix B: Detailed inorganic elemental analyses 83
Appendix C: Oil thermal analysis profiles (TG and DSC) 88

FIGURES

Page

1 Flow and valve labeling schematic 6
2 Photograph of liquefaction reactor system 7
3 Arrangement of thermocouples in reactor 11
4 Reaction temperature and pressure profile, Run RS 20

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TABLES

Page

1 Reactor testing experience 21
2 Elemental composition of Portland sludge 22
3 Initial results with Portland secondary sludge 22
4 Starting material and product composition, Run RS 23
5 Sludge feedstock composition 28
6 Sludge feedstock ultimate analysis 29
7 Sludge feedstock normalized ultimate organic analysis 30
8 Major inorganic elements in sludge feedstock 31
9 Water, heat, and ash contents of oil products 32
10 Major elemental compositions of product oils 33
11 Summarized inorganic element composition of product oils . . . 34
12 Volatilization of oils by thermogravimetry 36
13 Oil viscosities 37
14 **Pour point values for skimmed oils** 38
15 **Flash point values** 38
16 Char composition 40
17 Char ash analysis 41
18 Major inorganic elements in char 42
19 Product yields and production conditions 43
20 Mass/energy yields of oil and char products 47
21 Feed/product average elemental and ash contents 48
22 Feed/product average organic element contents 48
23 Feed/product organic element ratios 49
24 Ratios of C,H,N,O in products (feed as unity) 49
25 Selected inorganic elements in feed and products 51
26 Reactor off-gas composition 52
27 Wastewater analysis 53
28 COD and BOD of wastewater 54
29 Wastewater biodegradability 54
30 Dissolved solids ash content 55
31 Estimate bases for three STORS sizes 57
32 Purchased material cost estimate 61
33 Energy requirements and outputs of the sludge to oil facilities 62
34 **Cost estimate comparison for three different sizes of facilities** 63

SECTION I

INTRODUCTION

Disposal of sewage sludge is an increasing problem for many municipalities in the United States. A current need exists for implementation of alternative disposal technologies. At the same time, it is recognized that alternative technologies need to be energy-efficient, and that if possible, some product of value should be recovered from sludge. Direct thermochemical liquefaction has the capability of meeting all of these requirements.

Thermochemical liquefaction investigations by various authors over many years have shown that organic material can be converted to bitumen, heavy oil, and distillate oils with combustion heats approaching those of petroleum products. An organic solvent liquefaction process investigated on behalf of the U.S. Environmental Protection Agency (EPA) also proved capable of producing liquid fuels, but it was abandoned because of poor economics and the fact that it required a dry feedstock that had already solved the disposal problem (1).

The work reported here describes results from continuous liquefaction experiments using primary sewage sludge (20% solids) as feedstock. The sludge was converted to fuel oil and char products having 73% of the heat energy of the dry feed organic material, or 80% of the heat value of diesel fuel. Separation of products from the wastewater is envisioned as being spontaneous; coupled with the use of a wet feedstock, this makes the energy balance of the direct liquefaction process particularly favorable compared with incineration, for example.

At the beginning of this project, which was based on earlier autoclave (batch process) work to make a synthetic asphalt (2), we did not know if a continuous process would work, if useful products could be obtained, or if the overall process would be environmentally acceptable. Answers to these questions are all positive, but further research is needed before the technology can be efficiently commercialized.

SECTION 2

CONCLUSIONS

The results of experimental studies on primary sewage sludge liquefaction in a prototype continuous reactor have amply confirmed the feasibility of the process on a continuous scale for the production of fuel oil. The major objective of the project has therefore been met. New information has also been obtained on the behavior of aqueous primary sewage sludge slurries at elevated temperature and pressure. This information will be of value in designing the next generation of liquefaction reactors, as it significantly alters conventional assumptions about heat transfer, viscosity, corrosion, erosion, and char deposition during the process. As in previous batch studies, sludge liquefaction occurred rapidly above 265°C. Complete conversion to products (oil, char, and gas) occurred within 1.5 hr at 300°C, the shortest residence time achievable with the reactor in its present configuration.

Inspection of the reactor after more than 100 hr of operation showed that anticipated problems of char buildup on unscraped surfaces, corrosion, and plugging did not occur under the conditions used. This is a significant departure from previous experience, as for example with the wood liquefaction pilot plant at Albany, Oregon. Some erosion of teflon valve seals did occur, presumably because of high-velocity sand and ash particles, but this was solved by inclusion of a steel wool particle trap in the line. We conclude that corrosion, plugging, and erosion are not likely to be obstacles in further development of the liquefaction process.

Product mass and energy yields were high, with typically up to 36% yield of oil, 18% yield of char, and combined energy yields of 73% of feedstock heating value. Spontaneous product separation from wastewater did not occur in all experiments, requiring a solvent extraction for recovery of products. Later experiments performed with higher pressures of inert gas (nitrogen) did achieve spontaneous separation of a higher quality oil product from wastewater. Further work needs to be done on product separation to confirm this result.

BOD determinations were performed using an unadapted microbial seed from a local sewage treatment plant. The results suggest that the wastewater from the process would be highly biodegradable using an aerobic digestion. Byproduct gas was also a minor environmental pollution concern. Metal concentrations were as much as 27-fold lower in the product oil than in the starting sludge, but were more concentrated in the char. Any toxic organic materials produced in this process are likely to be concentrated in the oil, and would be destroyed during combustion. Disposal of ash from char combustion remains a potential problem.

The study performed a preliminary economic comparison of the liquefaction process with conventional incineration. Liquefaction appears to be economically more attractive, both on an initial capital investment and an operating cost basis, with, for example, a sludge disposal cost of $43/dry tonne for a city of 1 million, with a capital equipment cost of only $6.1 million.

SECTION 3

RECOMMENDATIONS

The project described in this report demonstrated the feasibility of the liquefaction process on a continuous scale. The optimism about this process expressed in our previous report was thus fully justified. We continue to feel that liquefaction offers a cost-effective alternative to incineration -- one that would be environmentally acceptable in practice. However, the behavior of the sludge at elevated temperature and pressure was unexpected. Based on our experience with the prototype, further work should be performed with a modified reactor, to refine the parameters for a pilot plant.

Further work should be done on product separation, based on the pressure effect, to ensure optimum product recovery and quality. Solvent extraction is unacceptable in a commercial process for sludge conversion to fuel. Spontaneous separation of oil and char was observed in some experiments and not in others, but a detailed examination of separation was outside the scope of this project.

Liquefaction has shown the potential for concentrating metals in the inorganic fraction of the char, and also for destroying organic materials through alkaline digestion. The potential of the liquefaction process as a novel technique for concentrating heavy metals and rendering organic wastes harmless should be studied further, and accurate data on mineral balances and destruction rates should be obtained.

An additional research project should be performed using a smaller-diameter reactor so that extended runs can be performed. With the use of sludge "spiked" with various metals and organic nonradioactive tracers, the work outlined here on process parameter refining, separation, and detoxification potential can be performed in a cost-effective manner.

SECTION 4

MATERIALS AND METHODS

REACTOR DESIGN

General

Specific engineering details of reactor design are proprietary, but the following general description, together with the diagram of the system (Figure 1.) and photograph (Figure 2) should provide a clear picture of the continuous liquefaction operation. The reactor is a 15 cm o.d. vertical stirred tube, with sludge injection from the bottom by means of a metering injection pump. The reactor is electrically heated, originally with a 13 kw ceramic heater wrapped around the lower 1.3 m of the reactor (the heating zone). In the original design, the middle 1.3 m was designated as the reaction zone and was not independently heated, while the upper 1.3 m was the cooling zone. Water cooling was used, and was achieved by means of coiled copper tube around the upper part of the cooling zone, prior to product exit from the reactor into the pressure let-down system. In practice, as indicated in the next section, the hot digesting sludge behaved as a very low viscosity fluid, so that plug flow was not achieved, and heat transfer occurred between the heating and cooling system. It was therefore necessary to install additional electrical heating capacity (8.4 kw) around the reaction zone and move the cooling off to the side. The system as it stands is capable of processing 144 kg/d of dry sludge (or 720 1/d of 20% solids sludge). This compares, for example, with the 1 1 scale batch reactors used in previous work by us and others (e.g., ref. 1).

To our knowledge this was the first time that the liquefaction process had been applied to primary sewage sludge, continuously, on this scale. Other continuous reactors in existence have used substrates such as wood or garbage, and hence have encountered somewhat different problems. Based on the experience with wood liquefaction at Albany, Oregon (3 ton/day pilot plant) and with bench scale work supporting this plant, we had expected problems with heat transfer, pumping a viscous slurry, corrosion, char build-up (coking) of the reactor walls, slow reaction times and a requirement for high temperatures. On the whole, the prototype reactor worked very well, although we were unable to reach the full range of reaction conditions originally designed for, due to unexpectedly low feed/reactant viscosities inside the reactor. Each of these factors will be briefly discussed, together with some suggestions for improvements or further work.

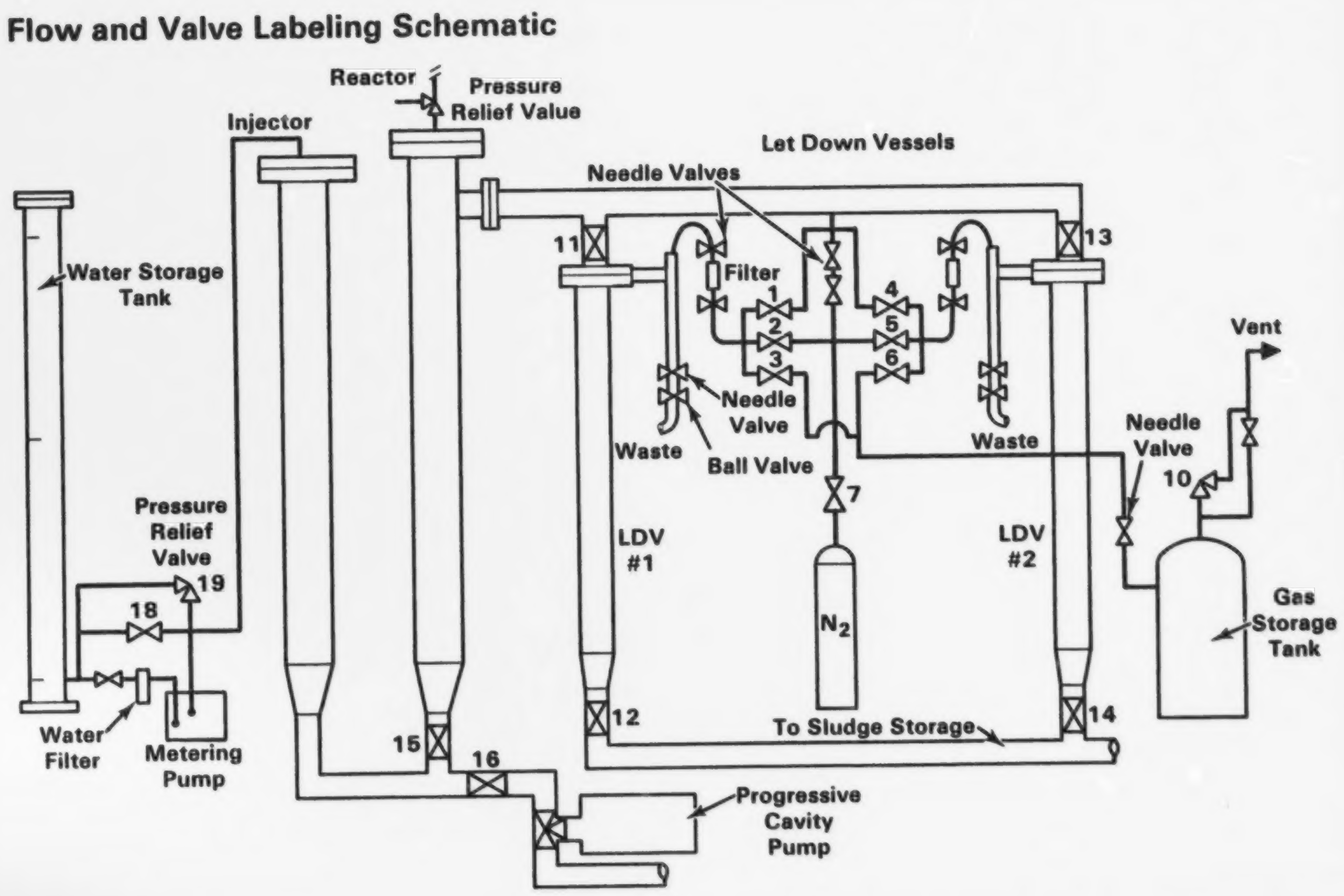


FIGURE 1. Flow and Valve Labeling Schematic

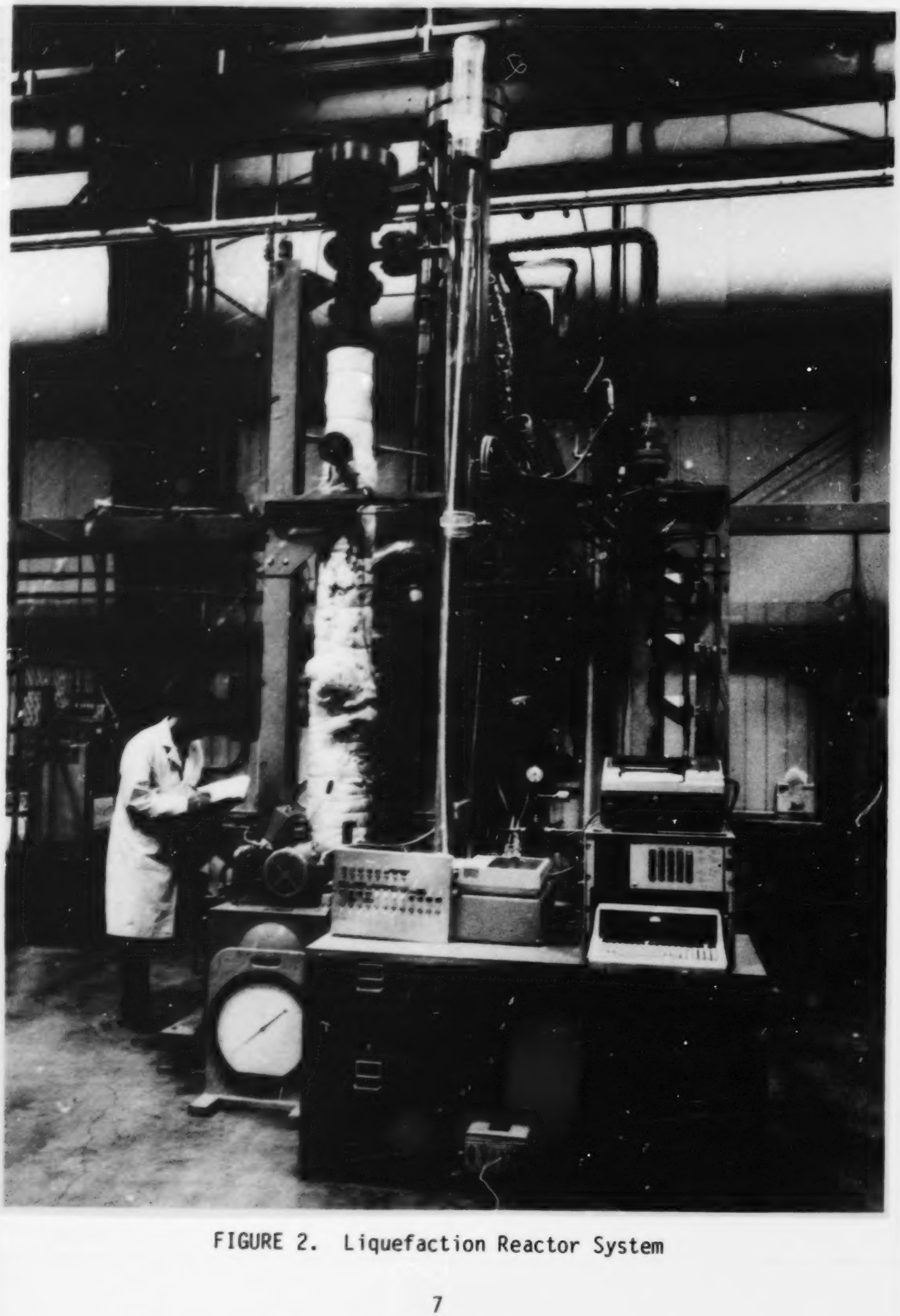


FIGURE 2. Liquefaction Reactor System

Size Criteria

The size of the reactor system was determined by considering many factors, including the desired volumetric flow, height of the crane in the Mechanical Development Laboratory (where the reactor was located), Washington State pressure vessel regulations, construction material availability, and Battelle's pressure system safety guidelines. For instance, to avoid strict and costly State codes the inside diameter of the pressure vessels had to be less than 6", the volume of each vessel less than 5 ft^3, and the thermal input less than 60 Kw. In considering all of these factors, a six inch nominal, double extra strong pipe (Schedule 160 XXS, wall thickness 0.864 in) emerged as the optimum shell for the pressure vessels.

A reactor system that was about 100 times smaller than the target pilot plant design of 3 tonnes/day was desired. This amounts to 30 kg/d. Since 8-12 hr shifts were anticipated, this increased the desired size to 60 kg per 8-12 hr day, or 7.5 kg/hr, corresponding to a volumetric flow rate of roughly 7 l/hr. The design residence times were to be 0.5 to 3 hr. This expanded the required volume for the 3 hr residence time to 21 l. Dividing this value by the required cross-sectional area of the 6 in pipe yielded a length of 1.7 m.

Based on this and the height constraints, the reactor heating zone, residence zone and cooling zone were each set at a length of 1.22 m (4 ft), giving the residence zone a gross volume of 0.014 m^3 or 14.7 l. This determined the metering pump capacity range as between 4.9 and 29.4 l/hr (the currently installed metering pump has a range of zero to 60 l/hr).

The injector and water storage vessel were sized to have essentially the same volume as the reactor, each let-down vessel having half the volume of the reactor.

The maximum heating system duty should have been equal to the enthalpy change of the sludge between 20 and 350°C plus losses. The maximum enthalpy change at the maximum flow rate was therefore expected to be approximately 12 Kw. A heating system rated at 13 Kw was specified initially.

It was assumed that the high viscosity of sludge would inhibit significant backmixing within the cooling zone and that the desired high temperatures could be reached. This turned out to be incorrect and heat loss by reflux was much greater than anticipated. The knowledge gained from this experience has led to design changes that will prevent this problem in the pilot plant.

Heat transfer

Scraped surface heat exchange was selected after consideration of immersion heaters and steam injection. Immersion heating was not selected due to concern over charring problems. Steam injection, in addition to being costly, would not work at high temperatures. External electric-fired radiant heaters were selected based on cost, reliability and accuracy of control.

The radiative heat transfer to the outside surface of the reactor is essentially instantaneous. The inside film coefficient of the scraped surface sludge is the slowest part of the heat transfer. The value of the heat transfer coefficient was estimated using equation 1.1:

$$hi = 2*(kpcnb/Pi)^{.5} \qquad 1.1$$

Where:
k = the thermal conductivity in $W/m^3{}^\circ C$
p = the density in g/m^3
c = the heat capacity in $J/g^2{}^\circ C$
n = the scraper rotation speed in rps
b = the number of blades
hi = the scraped surface inside coefficient $W/m^2{}^\circ C$

(Source: McCabe, 1967 (Reference 3)).

It is important to note that this inside heat transfer coefficient is independent of viscosity. This is important because the viscosity of the alkaline sludge as a function of temperature is unknown. Based on this correlation, it was determined that there would be sufficient heat transfer area to heat the sludge.

Hydraulic scraper system

A hydraulic motor was used inside the reactor to turn the scraper because mechanical seals were too costly due to the high temperatures anticipated. Early in the design stage it was decided to put the flange on the top of the reactor, for ease of maintenance and removal of the scraper. With the flange on top, the scraper could be removed and the reactor cleaned without dismantling the entire system.

The hydraulic system was designed to turn the scraper at an adjustable rate. A backpressure valve loaded by the headspace pressure was used to keep the pressure in the hydraulic motor higher than the pressure in the reactor. One of the key constraints was finding a hydraulic motor that would fit inside the reactor. Once a motor was identified, the system was sized based on the oil flow required by the motor at the desired speed and pressure.

Gas handling Sub-system

The gas line connections were the most complicated part of the system. The purpose of the gas lines was to control the reactor pressure and minimize the loss of high pressure nitrogen and reactor gas during the let-down operation.

The gas handling system consists of numerous needle valves, seven electric ball valves, a cascade of nitrogen supply tanks, a large gas receiving tank and an outside vent connection. There are three parts to the gas connections. The high pressure line conveys high pressure gas from the let-down vessel to the intermediate line. The needle valves act as orifices between the high pressure line and the intermediate line. The intermediate line conveys the gas to the low pressure let-down vessel. When both let-down vessels are at the desired pressure or during let-down operations, the storage tank access line is used.

In the original design and operation of the system, the reactor pressure was controlled by loading the dome of two back-pressure valves. The back-pressure valves worked well until the teflon diaphragm failed. Severe erosion of the diaphragm was caused by particles and vapor droplets passing through the orifice at sonic velocities. Several measures were taken to reduce this problem, including the installation of a dogleg liquid collector and stainless steel wool in-line filter. The doglegs were drained during reactor operation by manual control of the needle- and hand-operated ball valve at the bottom of the dogleg. The in-line filter has a needle valve at either end so that it can be cleaned during reactor operation. Problems with leaking back-pressure valves were still encountered. Finally, two needle valves in series were substituted for the back-pressure valves.

Control of the gas was accomplished by using the 7 electric ball valves and the needle valve on the line to the storage tank and the needle valves between the high pressure line and the intermediate line.

Reactor Instrumentation

The reactor instrumentation consisted of 19 thermocouples, 3 pressure gages and 4 pressure transducers. The pressure transducers were connected to the intermediate line, reactor headspace, injector water feed line and storage tank. The pressure gages were located on the storage tank, injector feed line, and a connecting line from the reactor headspace and intermediate line.

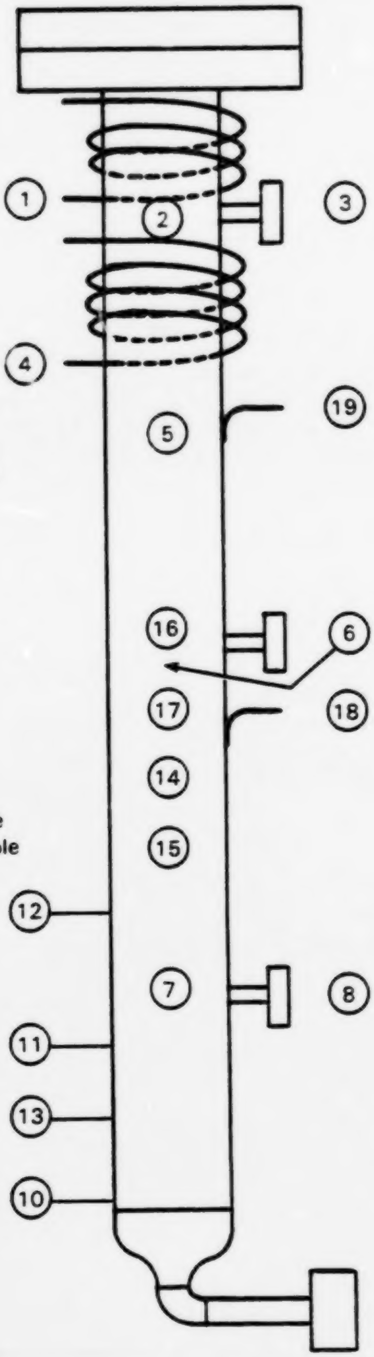
The data was collected and stored in a Hewlett-Packard data acquisition system with real time video display output. This information was used in conjunction with the gages to operate and control the reactor system.

Prior to a run we found it useful to leave the 24 V power supply on overnight so that the transducers and the power supply could stabilize. This reduced the amount of calibration necessary and improved accuracy. However, sometimes the pressure transducers would read low by about 25%. Light tapping with a copper tube "recalibrated" the transducers to the correct value. This observation is important because it helps to explain some of the low pressures indicated by the data traces of the early runs.

On leaving the reactor vessel, the hot pressurized reaction products passed into one of two pressure let-down vessels, after being cooled. A complex gas handling system was used to effect product transfer to a collection drum, control gases evolved from the reaction and pass them to a gas collection vessel, and maintain a safe condition in the reactor itself (by reducing boiling).

Figure 3 shows the arrangement of thermocouples on and in the reactor (#6 was used to monitor the nominal run temperature, since it was at the midpoint, inside the reactor).

Testing and modification of the reactor and its appurtenances was an important part of the research program. To avoid redundancy, details of the work are presented later in this report (Section 5).



1. Cooling water outlet
2. Outer vessel wall-top of reactor
3. Sludge-exit thermowell
4. Cooling water outlet
5. Outer vessel wall-top of insulation
6. Sludge-mid thermowell
7. Outer wall-lower thermowell
8. Sludge-lower thermowell
9. Product line (not shown)
10. Lower wall outer surface
11. Lower wall outer surface
12. Lower wall outer surface
13. Lower wall outer surface
14. Mid wall outer surface
15. Mid wall outer surface
16. Mid wall outer surface
17. Mid heater thermocouple
18. Main ceramic heater thermocouple
19. Supplementary heater thermocouple

FIGURE 3. Arrangement of Thermocouples in Reactor

SLUDGE FEEDSTOCK PREPARATION

The continuous liquefaction reactor was designed to operate with a 20% solids sludge feedstock, made alkaline with 5% of anhydrous sodium carbonate. The feedstock was required to have as high an organic content as possible, and hence to be a primary rather than a secondary sludge. The first portion of this task was to identify a local Washington state municipality with a supply of 20% solids sludge, or failing this, to obtain enough of a more dilute material for delivery to Battelle, where it would be dewatered. After investigation, the latter alternative was selected, as no readily available source of primary sludge of 20% solids content was available.

Initial shake-down tests on the reactor system were performed with water, with secondary sludge from Portland (67% ash, dry basis), and with secondary City of Richland sludge mixed with peat moss (48% ash, combined dry basis) to increase its organic content. Only after these tests were successfully completed was the primary settled and centrifuged Richland sludge passed into the reactor.

Primary settled sewage sludge from the City of Richland, WA, was delivered by truck to our Chemical Engineering Laboratory (CEL), where it was transferred to 55 gallon drums. This material was obtained in several batches, to minimize decomposition between runs. As quickly as possible after delivery, 1% polymer was stirred into a drum, and the contents transferred to a stirred holding tank for dewatering by centrifugation. The centrifuge was a Bird 6" continuous model capable of taking 6 gal/min. of 3-4% solids sludge and converting it to 18-20% solids material. The centrifuged sludge (20% solids) was mixed immediately with 5% by wet weight of solid anhydrous sodium carbonate, using the reactor feedstock progressive cavity pump in a recycle mode to ensure complete mixing. In this state, we observed no digestion or decomposition of the feedstock (which was at a pH too high for normal digestion) even in small samples kept at ambient temperatures for several weeks. The mixed sludge was a thick, black, homogeneous and gelatinous slurry which showed no indication of phase separation. It was re-mixed prior to injection into the reactor. Drums of feedstock were weighed and labeled after preparation.

ANALYTICAL METHODS

Sample Preparation

Bulk products obtained from continuous reactor experiments were collected in 55 gallon drums, clearly labeled with the date, project number, and run conditions. We attempted to use one drum of sludge feedstock and to collect one drum of products for each run; this corresponded to a rate of 12 gallons/3 hr (one reactor volume used for residence time basis), or an approximate run time of 14 hr. at a nominal 3 hr residence time. Each drum collected was thoroughly stirred, and a ca. 200 ml sample of the homogeneous product taken, placed in a glass jar, and transferred to the laboratory. The mixed sample was accurately weighed. The weight of the sample was obtained by weighing the empty jar. The mixed product containing water, oil, and char was extracted by dichloromethane in 3 x 100 ml aliquots, placed in a separatory funnel and shaken for about 5 min. The oil and char suspension/solution in dichloromethane was separated from the water phase. The water phase was evaporated and the residue weighed, ashed, and weighed again to obtain total solids, organics, and ash. The char was separated from the oil solution by mild centrifugation on a bench centrifuge at 3000 rpm for 5 min. The oil solution was poured off and evaporated at 20°C in a rotary evaporator. The char was air-dried and then dried in a 110°C oven overnight. Both oil and char were weighed to obtain yields.

Following collection of analytical samples from the vigorously stirred product immediately after completion of a run, these drums were stored at ambient temperatures until the separation of oil, aqueous phase, and char was deemed complete. Bulk products were extracted with dichloromethane, separated from aqueous phases, combined, and solvent removed. Oil, char, and aqueous phases were subjected to various analytical tests. As far as possible, standard methods and ASTM-approved procedures were used. Data obtained was recorded either in dated and signed laboratory notebooks or in a project file.

Results obtained corresponded to char and oil definitions as materials insoluble, and soluble in dichloromethane, respectively. In some measurements involving oil, a sample was physically skimmed off the surface of the settled product, and water decanted to leave the char. The latter char product contained considerable amounts of entrained oil and is therefore different from the char obtained by extraction. When such samples were used, they were carefully labeled as 'skimmed'. The symbol 's' following any sample designation in this report is used to distinguish skimmed oils and chars from extracted samples. Since in a commercial application of this technology we would plan to use skimming and decantation rather than solvent extraction for product separation, the comparison of results between skimmed and extracted products is of some value.

Gases evolved during the course of a run were collected in a gas collection vessel rated to 500 psig. A mid-run gas sample was taken for each run, and in some cases 2 samples were taken and analyzed by gas chromatography, in duplicate. The major components were nitrogen (used as a purge gas and pressure control for the reactor) and carbon dioxide (product from liquefaction). A log was kept of gas pressure in the collection vessel so that it was possible to determine the actual mass of each gas produced during a run. Some water and organic volatiles also condensed in the gas collection vessel and were periodically drained off.

One unanticipated result was the collection of a tar in the gas pressure relief system. This material was of low volatility and must have formed there from volatiles. The problem was solved by extension of the system with a dogleg attachment, which was periodically purged with nitrogen. The organic product was collected from one run and was designated as a 'dogleg sample'. It was small in quantity, and significant only from its potential to clog the relief valve arrangement.

SLUDGE ANALYSIS

City of Richland primary sewage sludge used for the liquefaction experiments was dewatered by centrifuging following addition of 1% polymer, and then addition of 5% by wet weight of anhydrous sodium carbonate. This material was analyzed for ash, water, fat, and heat content, and its elemental composition determined, as follows:

Ash Content

Prepared sludge (4-5 g) was accurately weighed and placed in a pre-fired porcelain crucible, which was then heated in an oven at 750°C for 1 hr. After cooling to room temperature in a desiccator, final weight was measured and the ash weight obtained by difference. The ash contents obtained are reported in the Results section as % ash in the sample. Duplicate analyses were performed.

Water Content

Water contents of sludges were obtained in a similar manner as for ash, but with heating only to 110°C overnight in a vacuum oven, followed by reweighing. Water content was obtained by difference and reported as % water in the sample. Total solids content and organic solids content were derived from water and ash contents by subtracting percent water from 100%, and by subtracting percent ash from the percent solids thus obtained, respectively. Duplicate analyses were performed.

Fat Content

An accurately weighed sample of dried sludge (obtained from the water content analysis above) was extracted in a dried Soxhlet thimble for 24 hr with dichloromethane. The extract was evaporated under reduced pressure at 40°C, and the last traces of solvent removed at 110°C in a vacuum oven for 5 min before reweighing. The weight of extract was obtained by subtracting the weight of the empty flask from the weight of flask plus extract. Duplicates were run, together with a control consisting of an empty Soxhlet thimble.

Heat Content

Heat contents of dried sludge samples were determined in duplicate by combustion in pressurized oxygen in a Parr bomb calorimeter according to ASTM D-3286-77, using benzoic acid as a standard.

Ultimate Elemental Analysis

Carbon, hydrogen, oxygen, and nitrogen contents of sludge samples were obtained in duplicate using a Perkin Elmer 240B elemental analyzer system. Oxygen was determined directly, not by difference. Sludge samples were dried at 110°C prior to analysis. Inorganic element components, including phosphorus and sulfur contents of oils were determined by X-ray fluorescence directly on the oil samples, according to the procedure described in Anal. Chem., 55(12), 1911-1914(1983); Ref. 4), rather than by the Inductively

Coupled Plasma technique originally proposed, for reasons of cost-effectiveness, and a higher sensitivity for sulfur and phosphorus.

OIL ANALYSIS

Oil is defined as dichloromethane-soluble material, after char removal, unless otherwise specified in the text as a "skimmed oil". Skimmed oil was removed physically from the surface of some products for viscosity, ash, pour point and other measurements. The following measurements were made on the oils from the continuous liquefaction runs 208-509 or from combined oil from runs 208-313:

* Water content
* Elemental analysis (C,H,N,O)
* X-ray fluorescence analysis (S,P, metals)
* Heat content (ASTM-D3286-77)
* Ash content
* Fractional distillation
* Thermogravimetry (in air and nitrogen)
* Differential scanning calorimetry (in air and helium)
* Viscosity, flash point, pour point

A cetane value engine test (ASTM D-613-79) was planned, but it proved impracticable to separate char and oil from the combined bulk product, since this was obtained before a method was found to achieve spontaneous char/oil separation. The combined product was deemed too viscous for the test, having apparently thickened during storage at outside ambient temperatures for 6 months.

Analyses were performed as described below:

Water Content

The method we planned to use (based on hydrolysis of 2,2-dimethoxypropane to acetone and GC measurement of acetone) proved to be too erratic in practice with these oils; we substituted water measurement on a Karl-Fischer apparatus (Photovolt Corp, Aquatest IV), which gave much more reproducible results.

Elemental Analysis

This was performed exactly as for the sludge feedstock, using the techniques already described (Elemental analyzer and X-ray fluorescence).

Heat Content

This was performed exactly as for the sludge feedstock, by ASTM D-3286-77.

Ash Content

This was also performed by the same technique already described for the sludge feedstock.

Fractional Distillation

Fractional distillation was performed on a composite oil from runs 208, 305, 306, and 313 (designated 'bulk oil' since it was exhaustively methanol extracted from the whole product from these runs, and was intended for use in the fuel quality test). The test was performed using the apparatus of ASTM D-1160.

Thermogravimetry and Differential Scanning Calorimetry

To broaden the range of information available on distillation properties of the products, thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis was performed on oils from individual runs. TG analyses were performed between 30 and 630°C in air and in helium, while DSC was performed over the same temperature range in air and nitrogen.

Viscosity

Oil viscosities were measured on a Brookfield LVT viscometer equipped with a small-sample adapter, sample jacket, and a Brookfield EX-200 temperature-controlled water bath. All measurements were made at 50°C, using spindles 18 and 34 and speeds of 0.3 - 60 rpm. This apparatus is limited to viscosities of 10,000 cp or less.

Pour Point

Pour points of oils were determined according to ASTM D-97, involving heating in an oil bath without stirring, for extracted oil samples. Skimmed oils flowed more easily, and so their pour points were determined by the method of cooling to the lowest temperature which still permitted flow (also ASTM D-97).

Flash Point

Flash points were determined using the apparatus and technique described in ASTM D-396-79.

CHAR ANALYSIS

Char yield, ash content, and elemental analysis were all performed using the same techniques already described for the sludge and oil samples. One additional test - combustion - was performed on char derived from the extraction of combined oil from runs 208-313.

Char Combustion Test

A char sample (about 10 g) was accurately weighed and heated in a crucible. Combustion behavior was observed, including ease of ignition, type of burning (flaming or glowing combustion), and ease of sustained combustion. Ash residue weight was determined. The purpose of this test was to permit evaluation of the char as an energy source for the liquefaction process.

GAS ANALYSIS

Gas samples obtained during a run were collected in gastight mylar bags and transferred to the laboratory for duplicate analysis on a Carle 3114 gas chromatograph equipped with a data processing system. Because of the large amount of diluent nitrogen present in the samples, the accuracy of analysis of trace gases was reduced.

WASTEWATER ANALYSIS

Analysis of the wastewater from the liquefaction runs was to include BOD, COD, suspended solids, evaporation residue, pH, and dichloromethane extraction on selected samples, rather than on samples from every run. Some additional data was obtained to better quantify the nature of the wastewater from the liquefaction process.

Solvent Extraction

Wastewater samples from 3 selected runs (100 ml each, in duplicate) were extracted in a separatory funnel with 3 x 50 ml aliquots of dichloromethane. The weights of solvent-extractable material were obtained by evaporation of the solvent under reduced pressure in a weighed round-bottom flask, reweighing with the extract, and taking the difference.

Suspended Solids

Water samples (100 ml) were filtered through previously weighed and thoroughly dried quartz microfiber filters under vacuum. After drying the filter and collected insoluble material at 100°C/1 hr under vacuum, the residue weight was determined. This corresponds to 'char' suspended in the water.

Evaporation residue

The aqueous phases from solvent extraction were filtered and evaporated under reduced pressure in a rotary evaporator, using a previously weighed, dry round bottom flask. Evaporation residue was then determined after completely drying the material and flask at 110°C for 1 hr under vacuum and reweighing.

pH Measurement

This was done using a standard pH meter and reference buffer for calibration.

COD Measurement

The wastewaters from these experiments were heavily loaded with organics. After a series of trials, it was found that a 1:200 dilution gave the best results. Standard COD determination technique was used: A 50.0 ml water sample (diluted) was oxidized by 25.0 ml of potassium dichromate (0.250 N) under 2 hr reflux. The solution was then back-titrated with ferrous ammonium sulfate hexahydrate to determine the amount of unreduced dichromate. Subtraction of results from a 50.0 ml water blank gave the results shown in the next section.

BOD Measurement

After initial experiments, a 1:8000 and 1:12,000 dilution of the wastewater was used for BOD determinations. A standard microbial seed was obtained from the Richland sewage treatment plant and diluted by 100, 50, and 25-fold. Combination of the seed dilutions with the two wastewater dilutions gave six determinations for each of the 3 wastewater samples examined. The initial dissolved oxygen concentration was determined with an oxygen electrode for these samples and also for 3 standards consisting of glucose/glutamine solutions with seed (same dilutions as above), and 3 blanks consisting of diluted seed in water. Samples were incubated for 5 days at 20°C and the final dissolved oxygen concentration determined. 'Biodegradability' of organic material in wastewater was determined as the ratio of BOD:COD expressed as a percentage.

Dissolved Solids and Ash Contents

In addition to the above data aqueous evaporation residue (dissolved solids), and ash contents were determined for runs 418 and 502-509 to enable us to better determine mineral balance and overall mass distribution during liquefaction.

Anaerobic Digestion

Two attempts were made to obtain measurable degradation of organic wastewater components under anaerobic conditions. In the first, a 4 l fermenter was loaded with 2 l water, 3.3 g of fresh, 20% solids sludge seed, and 10 ml of Run #313 wastewater, sparged with nitrogen, and stirred for 1 week. In the second, a series of bottles was set up according to the procedure of Shelton and Tiedje (Ref. 5), using a volume of wastewater calculated to provide a concentration of organic solids of 50 mg/l. Theoretical gas evolution from a glucose control was 4.7 ml.

SECTION 5

RESULTS AND DISCUSSION

REACTOR TESTING

A first sample of sludge was obtained from the Portland facility to use in reactor testing. This material was fully digested secondary sludge and contained 68% of ash. It was felt that if the reactor could be operated with such low-organic material, there would be little difficulty with sludge with a higher organics, lower ash content.

Fabrication of the reactor was complete in July, 1983. Hydro-testing at the fabricators was performed on the complete reactor assembly, to 2.6 x 106 kg/m^2 (3750 psi) with no leaks being detected. The system was then dismantled, transported to our Materials Development Laboratory (MDL), and reassembled, together with all power, water, and other supply lines and instrumentation. A repeat hydrostatic test was performed and the reactor system readied for startup testing. A series of initial problems developed, as anticipated in a prototype system, and were dealt with. These problems, and their solutions, are listed in Table 1. The reactor assembly was then taken apart for a detailed inspection and replacement of stirrer blades in a new configuration, on the basis of what was learned from two testing runs with Portland sludge. The composition of the Portland secondary digested sludge starting material is shown in Table 2, while Table 3 gives experimental results from the liquefaction run at 250°C.

The problem of achieving a reactor temperature of above 250°C was believed due to our use of a "low viscosity" feedstock. After installation of additional heating capacity, one additional reactor test run was performed on November 11, 1983, with the purpose of determining if there would be the same heating problem with a thick sludge as with a free-flowing sludge (i.e., Portland secondary). Since a suitable source of primary sludge was not available at the time, a thicker feed was simulated by mixing peat moss into Richland secondary sludge. The sludge/peat moss mixture had the composition shown in Table 4. Starting material was preheated in the reactor overnight, at 100°C. The next day a continuous run (the first), was begun, maintaining a maximum temperature at the top of the heating zone of 320°C, with a residence time of 16% of pump capacity (approx. 3 hr). The run was terminated after 3 hr of continuous flow, and sample products analyzed. (Because the amount of material passed through was relatively small, no material balance was attempted). The temperature and pressure condition readout from the pressure transducers and thermocouples is shown in Figure 4, as an example. Similar

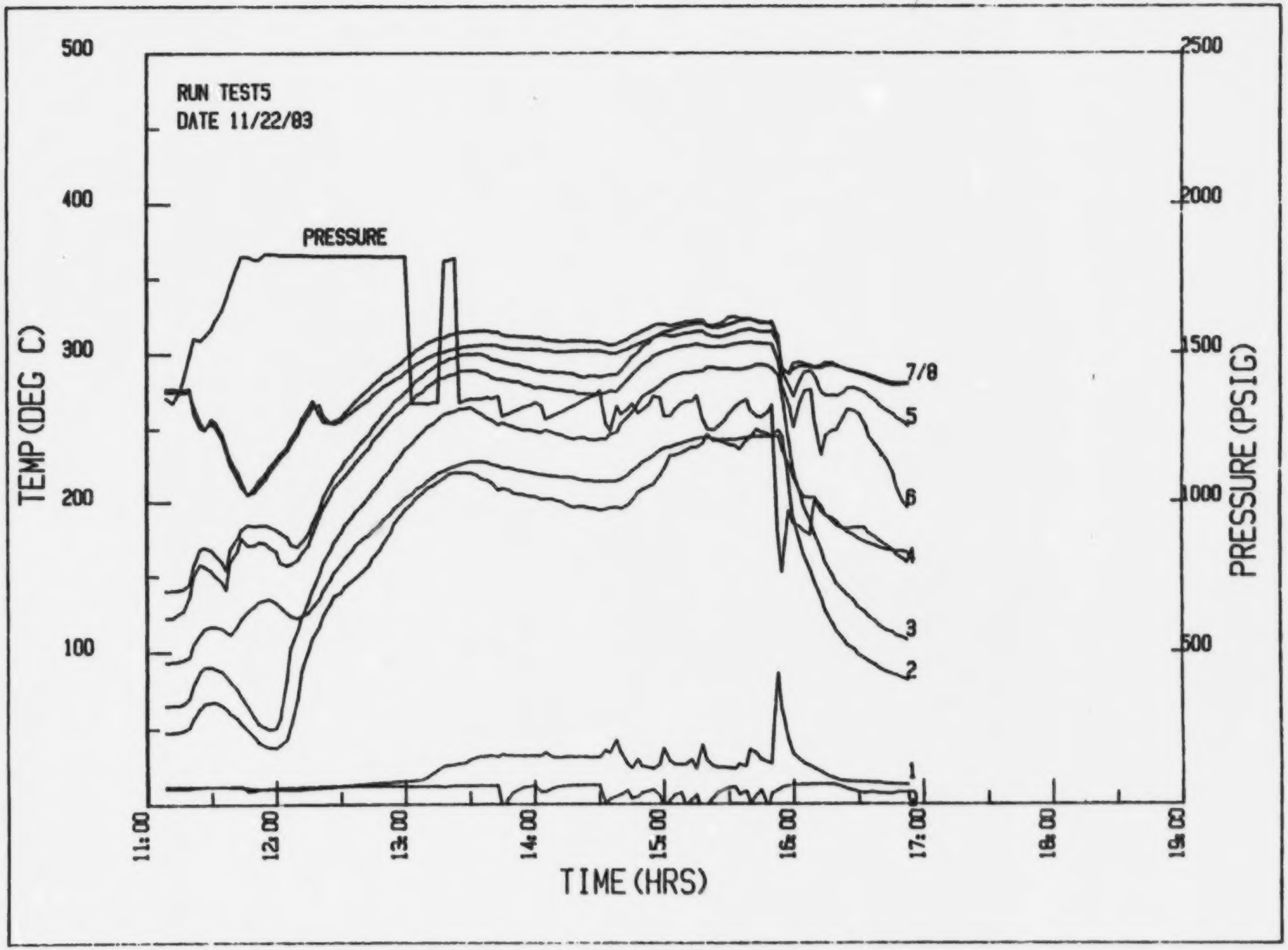


FIGURE 4. Reaction Temperature and Pressure Profile, Run RS

data from other runs is given in Appendix A1-A8. The analytical results on the products are also shown in Table 4. Oil was produced during this run, together with some char. The experiment was designated as Run RS, and all samples labeled with this prefix.

TABLE 1. REACTOR TESTING EXPERIENCE

Item	Problem	Solution
1	Sludge injection piston would not move smoothly.	Steel piston replaced by nylon.
2	Data Acquisition System (DAS) inoperative.	Return faulty board with system to manufacturer for correction.
3	Insufficiently high temperature achievable.	Drain water and inject sludge slurry directly.
4	Excessive wall temperature reached (950°C); unexpected because of thermocouple within 15 cm and wall thickness 2.5 cm.	Battelle materials experts consulted; reactor re-annealed in place; thermocouple re-sited.
5	Thermowell failed at 106 kg/m^2 (1450 psi) and 250°C.	Emergency shutdown. Hydraulic pump had been installed backwards, breaking thermowell. Pump direction reversed and thermowell replaced.
6	Maximum reactor temperature of 250°C achievable instead of design 370°C.	Caused by convection currents, heat transfer to cooling coils, rapid reduction of sludge viscosity on heating. Alleviated by removal of central scraper blades, resiting cooling coils, adding extra 8.3 kw heating.
7	Scraper assembly bent.	Result of hydraulic motor reversal. Blades replaced.

TABLE 2. ELEMENTAL COMPOSITION OF PORTLAND SLUDGE

Element, %	C	H	N	O*	S	P	Si	Fe	Al	Ca	Na
%	23.3	3.7	2.2	14.1	0.3	1.8	17.5	3.6	4.8	2.6	1.5

* Determined directly; not by difference.

TABLE 3. INITIAL RESULTS WITH PORTLAND SECONDARY SLUDGE

	Sludge	Product
Moisture (%)	68.2	60
Ash (wet, %)	21.6	23
Ash (dry, %)	68	58
Heat Content*	5300 +/- 400 (cal/g)	8100
pH	7.3	-
Distillate (ml)		
37-38 °C	-	0.5
80-90+	-	4.8
90-95	-	1.8

* Moisture, ash-free.
+ Contained dibutyl phthalate (plasticizer)

TABLE 4. STARTING MATERIAL AND PRODUCT COMPOSITIONS, RUN RS

Material	C	H	N	Ash
Richland sec. sludge	21.3	3.0	2.3	-
	22.6	3.1	2.6	-
Peat moss	48.9	5.1	0.7	-
	47.6	5.0	0.6	-
Sludge + Peat Moss*	26.4	3.1	1.3	51.0
	26.7	3.1	1.2	49.8
Sludge + Peat Moss	27.2	3.2	0.2	45.5
	29.3	3.5	0.0	45.7
Char from LDV #1	32.5	8.1	1.0	-
	30.7	8.1	0.8	-
Char from LDV #2	38.4	6.2	2.0	-
	37.2	6.1	1.2	-
Oil from LDV #2	76.2	10.1	2.2	-0-
	73.5	10.1	2.1	-0-

+ LDV = Let-down vessel.

* Percentage of dichloromethane extractable material in the starting material was less than 1% (i.e., fats and oils). Percentages of dichloromethane-soluble materials in char from LDV#1 and LDV#2 were 24% and 37%, respectively.

REACTOR OPERATING EXPERIENCE

The first full experimental run with centrifuged primary Richland sludge was begun on Wednesday, February 8 at a nominal 305°C and 1.5 hr residence time (designated Run 208). The term "nominal" is used because the temperature varied at different parts of the reaction zone, and residence time depends on the density of water at reaction temperature, definition of reaction zone, etc. Thermocouple #6 (Figure 3) was used as the temperature set point, in the center of the sludge just above the main heaters. Temperature varied somewhat during the run, as shown in the profile (Appendix A-1). Residence time was defined as (time x reactor vol.)/(vol. product), or 190 l of total product in 6 hr from a reactor volume of 45.4 l.

Using the above definitions for temperature and residence time, the run was completely successful with no problems, and with total feed conversion to product.

Based on this result, with total feedstock conversion at 300°C, it appeared that our original design assumption of 350°C was conservative, and that on a commercial design a much lower operating temperature could be used. However, we continued to try to meet the original design criteria.

On February 9, the reactor was started up again to start a second run with Richland sludge. We quickly experienced a problem with a blockage in the sludge injection to the injector from the drum. This was cleared (into the line) by reversing the valve on the injection point from the sludge pump. (Preheating the sludge did not appear to work well, because unless there is continual stirring, sludge dries out on the drum walls and either chars or dries, forming lumps).

The blockage was cleared, and the reactor started heating without any more problems. We could not get above 305°C even with no throughput, so this was the maximum temperature with the reactor in its configuration at that time. Having decided that we could not reach 320°C, we decided to try for the lower residence time, while monitoring the letdown vessel valve temperature. We collected about 20 l of product at 300°C and 0.75 hr nominal residence time, before we decided that the valve was getting too hot. This was not considered as "Run #2" because it was run at 300°C (not a set temperature) and only 20 l were collected, with no gas analysis possible.

It was also at this point that the plug from the injector, which should have passed through without problem, plugged the injection line into the reactor. The reactor was shut down, as we felt we had no chance of clearing this safely while running. This was also a good point to inspect the reactor, replace valve seals, and install additional heating capacity. This was done by rewiring the existing upper wall heaters and adding additional reactor insulation.

On March 5, the reactor was started up again, at 14:00, following sludge and reactor preparation. Appendix A2-A3 shows the temperature and pressure profiles for this run, which was the longest one completed to date (29 hr). During the run, two sets of conditions were maintained: 275°C/3 hr (EPA 305) and 305°C/3 hr (EPA 306), and two drums of products were collected. Product collected during changeover from one condition to another, and while heating and cooling the reactor, were collected separately in a combined "intermediate products" drum and were not included in the steady-state products collected.

After this long run, a planned shutdown took place. The reactor was still behaving well. A further run, EPA 313 (275°C/1.5 hr) was completed successfully on March 13 (Appendix A-4).

Run 418 (Appendix A5) was begun on April 18 at 8:45 a.m. and terminated at 23:20 after filling one 55-gallon drum with products. Operational temperature was 275°C with a 1.5 hr residence time. No problems were encountered.

Run 502 (Appendix A6) was begun on May 2, under the same nominal reaction conditions as Run 418, and continued for about 14 hr before a plug developed in the bottom of the reactor and the run was terminated. This was the first time a reactor plug caused a shutdown. Run 507 (Appendix A7) was the continuation of Run 502, and proceeded similarly, except that an emergency shutdown had to be performed due to a ruptured diaphragm in the hydraulic system. Neither of these events was serious in itself, but required shutdown for correction. The run was completed on May 9 (Run 509) (Appendix A8), after a total of 7 samples had been collected. Completion of this run also completed Task 1.

Comments:

Runs 208-313 in the continuous reactor demonstrated the essentially complete conversion of sludge to oil, char, water-soluble organics, and gas at temperatures as low as 275°C, with energy yields of char and oil combined of up to 73% (as shown by the yield calculations on p. 44). However, the spontaneous separation of oil and char from the wastewater which was observed during autoclave experiments did not always occur with the continuous reactor products. After discussion of the various possible reasons for this, it was decided to perform subsequent runs with an increased nitrogen overpressure, to determine whether this would improve separation. Run 418 was the first in which this was attempted, with good success. In Runs 502-509, we endeavored to establish the effect on a reproducible basis, again successfully. Product separation occurred spontaneously within 24 hr in most cases, although some oil was still entrained with the char. The wastewater was a transparent light brown. Because samples were taken more frequently than normal, although there was at least one letdown vessel volume of product collected between samples, equilibrium conditions were not attained at each sampling step. Also, in sample 507-6A, the product remained in the letdown vessel much longer than normal at the end of a run.

Although it was our original intention to obtain mass balances in bulk, through relating weight of sludge input to weights of products out, the fact that we did not have plug flow as anticipated originally made this impossible to achieve. The sludge/water/gas/product mixture in the reactor at temperatures above 275°C behaved as a liquid of very low viscosity. A calculation based on gas production during Run 208 and shown below indicated that the dissolved and undissolved gas concentration in the reactor corresponded to about 1.3 times the reactor volume at STP:

Gas Production Rate Calculation:

Logbook entry: 40.9 psi at time 1, temp. = 316°K
83.2 psi at time 2 + 20 min

Reactor volume: 45.42 l (12 gal)
Gas tank volume: 492.05 l (130 gal)

Gas produced in 20 min = (83.2/40.9) x 492.05 l at 316°K

= 998.9 l at 316°K

= 2997 l/hr at 573°K and 1 atm.

= 40.25 l at 573°K (300°C) and 135 atm.

Sludge flow: 45.42 l/1.5 hr, = 30.28 l/hr

Gas volume = 40.25/30.28, = 1.33 x Sludge volume.

Coupled with the fact the reacting sludge no longer behaved as a thermoplastic fluid, this means that effectively the reactor was a stirred tank. Hence, with the volumes of sludge passed through and with time and funding constraints, steady state conditions were not achieved and samples obtained cannot be directly related to input sludge. To obtain steady state conditions with systems such as this, it is our experience that between 5-10 full reactor volumes have to be passed through under one set of reaction conditions, whereas we had planned for allowing one 'intermediate' reactor volume of products between samples for every change of conditions. Further work with a smaller diameter reactor would allow us to obtain steady state mass balance results. For present purposes, small (ca. 200 ml) samples were taken from the drums of thoroughly stirred collected products, and were used for analysis. Bulk products were separated as described in the Materials and Methods section.

DISCUSSION OF REACTOR OPERATION

Corrosion and char build-up

Operation of a liquefaction reactor with sewage sludge at high pressure, temperature, and under alkaline conditions required careful selection of reactor material, to avoid the problems of stress corrosion cracking caused by chlorides and alkali. Another potential problem with reactor material occurred when hydrogen in excess of anticipated values was produced during the first runs. Hydrogen can cause embrittlement of steel under certain conditions. In this case we determined that the amounts were still too small for this to become a problem. However, potential corrosion was a concern, and the reactor walls were carefully checked, together with the scraper assembly, whenever the reactor was opened. At no time was any sign of corrosion noted, even on surfaces which were not scraped. Also, there was no build-up of char or coke on any heated surface, during the approximately 100 hours of reactor operation. Our tentative conclusion is that corrosion and coking should not present a problem in commercial practice, provided that reactor materials are carefully selected.

Erosion

One problem which did occur to some extent was that of erosion of teflon seals on the pressure relief valves, caused by high velocity mineral particles entrapped in the out-flowing gas. It is possible that these particles helped inside the reactor to prevent coking, by their abrasive action. They were a nuisance in the gas lines until a steel wool trap was used to filter them out. Future designs will need to be evolved that can take care of sand particles traveling at high velocity.

Heat transfer

1. Reactor heating - According to the original design, plug flow of sludge and products would occur inside the reactor due to the high viscosity, narrow diameter, and slow upward movement of the feed. Horizontal heat transfer would occur through the scraped stirrer blades, which would cause effective transverse mixing between the wall and the cooler center of the reactor. On passing upward through the heating zone and the reaction zone, the products would be cooled by the water cooling coils wrapped around the top third of the reactor. This whole theory was based on an assumption of a relatively high

viscosity of feed and products, and seemed reasonable even though little was (and is) known about sludge behavior at elevated temperatures. In fact, repeated discussions between the project staff and experienced sanitary engineers failed to raise any concerns that the sludge would not behave as expected. Reactor design was reviewed by our industrial sponsor, Battelle safety engineers, and others prior to construction. In view of our experience to the contrary, the actual behavior of hot sludge inside the reactor should be taken as a contribution to sludge engineering technology. The material behaved as a very low viscosity fluid as soon as reaction temperature was reached (about 265°C), and further designs for liquefaction reactors should be based on this fact. Total mixing occurred between incoming sludge and products, and was easily observed on the thermocouple readouts, as temperature excursions between upper and lower parts of the reactor were frequent and significant. In some cases, the heaters had to be turned off for several minutes while the reactor continued to heat up without additional heat input; in other cases, cooling occurred with heaters on maximum. Control of the reactor under these circumstances was a matter of operator skill. However, there was no danger of uncontrollable overheating as the reactor had been designed completely fail-safe, and the liquefaction reactions take place endothermically.

Because of the vertical reactor configuration, there was little that could be done to modify the reactor so as to achieve its original design temperature of 350°C. By putting in additional heating capacity, moving the cooling coils over to the side, removing the central stirrer blades, and adding wall insulation to the top of the reactor, we were able to raise the maximum achievable temperature to, in one case, 320°C, although normal operating maximum was 305°C. The mobility of the reactor contents caused a designed plug flow to become a stirred tank reactor. This did not interfere with achievement of project objectives, but raises design questions for the future. Use of a narrow diameter, tilted or horizontal reactor would minimize vertical mixing and heat transfer problems, but would increase overall reactor length. This question needs to be studied in more detail.

2. Product cooling - As a result of the mixing of reactants vertically in the reactor, cooling of products prior to entry into the let-down vessels became a problem. The pressure valve between the reactor and the let-down vessel was rated at below 100°C because of the plastic internal seal. The connection between the top of the reactor and the entrance to the valve was a 1.8 m length of 5 cm o.d. steel tube. This was wrapped with copper cooling coils, but the cooling capacity was inadequate to maintain the 100 degree maximum outlet temperature required, except at low flow rates. Originally, residence time in the reactor was defined as the time required for a particle to pass into and out of the reaction zone - one third of the reactor length. Because of mixing, the whole reactor had to be redefined as the reaction zone, so that a 3 hr. residence time by the original definition became a 9 hr. residence time by the new, and realistic definition. As it turned out, a 1.5 hr. residence time was quite adequate for complete liquefaction to occur (corresponding to 0.5 hr. by the original definition). This was an excellent result in that the liquefaction was complete in a third of the minimum time previously considered likely, but it raised problems with sludge flow and product cooling. Future designs will require much more cooling capacity and

higher flow rates through the reactor, or replacement of the let-down valves with more temperature resistant (and expensive) varieties.

SLUDGE COMPOSITION

The sludge starting material was extensively analyzed so that product compositions could be related back to the feed. The following tables (Tables 5-8) present the results of sludge analysis. More detailed analytical data on trace elements in the feedstock is given in the Appendix (B-1). A discussion of the effects of liquefaction on feed and product compositions and chemistry follows the data on major product analysis (oil and char; p. 43).

TABLE 5: SLUDGE FEEDSTOCK COMPOSITION

Run #	Water %	Solids %	Organics %	Ash %	Fat %	Heat Value* Measured cal/g		Heat Value* Average cal/g
208	79.27	20.73	65.26	34.74	9.61	3189	-	-
305	76.42	23.58	66.07	33.93	2.25	2961	2943	2952
306	81.16	18.84	64.33	35.67	3.67	3295	3285	3290
313	80.22	19.78	65.37	34.63	3.80	3356	3293	3325
418 #1	79.23	18.77	67.95	32.05	3.51	3040	3063	3052
418 #2	79.78	20.22	65.92	34.08	4.14	3224	3288	3256
502-1	79.79	20.21	62.26	37.74	2.76	2872	3004	2838
502-2	Same feed as 502-1							
502-3A	79.41	20.59	61.33	38.67	2.73	2725	3013	2869
507-4	79.82	20.18	62.81	37.19	2.76	3109	-	-
507-5	Same feed as 507-4							
507-6A	79.33	20.67	62.81	37.19	2.94	2944	2948	2946
509-6	80.60	19.40	65.19	34.81	3.39	3216	3144	3180
Blank	-	-	-	-	0.00	-	-	-
	-	-	-	-	0.04	-	-	-
Benzoic acid used as standard:						6333(measured) 6318 (actual)		

* To convert cal/g to BTU/lb dry sludge, multiply by 1.8

TABLE 6: SLUDGE FEEDSTOCK ULTIMATE ANALYSIS

Run #	C %	H %	N %	O %
208	38.80, 39.0	5.51, 5.78	1.72, 2.02	24.61, 20.03
305	29.74, 31.38	3.93, 4.50	1.05, 1.45	30.98, 28.61
306	33.98, 35.01	4.48, 4.78	1.62, 1.89	29.03, 29.58
313	33.20, 33.05	5.05, 5.10	1.86, 1.84	29.35, 30.76
418 Drum #1	32.05, 33.80	4.66, 4.82	0.90, 1.35	27.71, 25.57
Drum #2	31.24, 31.94	4.43, 4.46	1.14, 1.20	27.64, 25.71
502-1	23.76, 29.66	3.52, 4.31	0.11, 0.73	23.53, 26.59
502-2	Same feed as 502-1			
502-3A	22.64, 27.66	4.58, 4.44	1.00, 1.04	26.06, 26.88
507-4	34.12, 30.44	5.08, 4.58	1.01, 1.07	27.52, 23.87
507-5	Same feed as 507-4			
507-6A	28.62, 29.76	4.81, 4.48	1.08, 0.89	28.32, 27.18
509-6	32.42, 30.92	4.77, 4.78	1.20, 1.07	27.10, 28.37
Cellulose	41.87, 42.12	6.21, 6.23	-0- -0-	45.51, 45.38
Cellulose, actual	41.62	5.82	-0-	46.20

Oxygen determined directly, not by difference.

TABLE 7. SLUDGE FEEDSTOCK NORMALIZED ULTIMATE ORGANIC ANALYSIS*

Run #	C %	H %	N %	O %	Ash %
208	59.66	8.66	2.87	34.20	34.74
	(38.94)	(5.65)	(1.87)	(22.32)	
305	46.25	6.39	1.89	45.10	33.93
	(30.56)	(4.22)	(1.25)	(29.80)	
306	53.63	7.20	2.74	45.66	35.67
	(34.50)	(4.63)	(1.76)	(29.31)	
313	50.68	7.77	2.83	45.98	34.63
	(33.13)	(5.08)	(1.85)	(30.06)	
418	48.20	6.86	1.72	39.83	33.07
	(32.26)	(4.59)	(1.15)	(26.66)	
502-1	42.90	6.30	0.67	40.25	37.74
	(26.71)	(3.92)	(0.42)	(25.06)	
502-3A	41.01	7.35	1.66	43.16	38.67
	(25.15)	(4.51)	(1.02)	(26.47)	
507-4	51.39	7.69	1.66	40.92	37.19
	(32.28)	(4.83)	(1.04)	(25.70)	
507-6A	46.47	7.40	0.72	44.18	37.19
	(29.19)	(4.65)	(0.45)	(27.75)	
509-6	48.58	7.33	1.75	42.55	34.81
	(31.67)	(4.78)	(1.14)	(27.74)	
Overall average:	48.88	7.30	1.85	42.17	35.76
	(31.44)	(4.69)	(1.20)	(27.09)	

* Adjusted to averaged, dry ash-free organic basis. Ash-included basis values in parentheses.

TABLE 8. MAJOR INORGANIC ELEMENTS IN SLUDGE FEEDSTOCK

	Elemental Concentration, %, +/- probable error								
Run†	Al	Si	P	S	Cl	K	Ca	Ti	Fe
208	0.705‡	2.69	1.254	0.905	0.147	0.309	4.57	0.187	1.188
	0.089	0.15	0.071	0.048	0.009	0.016	0.23	0.010	0.059
305	0.425	2.60	0.947	0.744	0.099	0.164	1.881	0.102	0.908
	0.078	0.14	0.050	0.040	0.007	0.009	0.094	0.005	0.045
306	0.352	2.03	0.845	0.612	0.070	0.150	1.979	0.106	0.783
	0.072	0.11	0.050	0.033	0.005	0.008	0.009	0.006	0.039
313	0.139	1.573	0.768	0.608	0.071	0.144	2.11	0.096	0.660
	0.071	0.093	0.047	0.033	0.006	0.008	0.11	0.005	0.033
418	0.674	2.11	0.792	0.687	0.093	0.169	2.25	0.113	0.848
#1	0.091	0.12	0.050	0.038	0.007	0.009	0.11	0.006	0.042
418	0.534	1.615	0.801	0.709	0.113	0.173	2.09	0.112	0.827
#2	0.079	0.095	0.040	0.039	0.007	0.009	0.10	0.006	0.041
502	0.309	1.90	0.749	0.663	0.107	0.168	1.932	0.109	0.793
-3A	0.075	0.11	0.046	0.036	0.007	0.009	0.097	0.006	0.040
507	0.233	1.671	0.700	0.664	0.110	0.168	1.921	0.111	0.722
-4	0.070	0.096	0.043	0.036	0.007	0.009	0.096	0.006	0.036
509	0.425	2.28	0.791	0.655	0.107	0.187	2.27	0.115	0.818
-6	0.078	0.13	0.048	0.036	0.007	0.010	0.11	0.006	0.041

* Not all sludge samples analyzed for inorganics;

† IAEA Soil-5, 1633A Flyash, and NBS Coal used as standards - complete analysis for comparison is given in Table 9;

‡ Ti source values, except Ti, Fe, used Zr source.

OIL COMPOSITION

Oil is defined as dichloromethane-soluble material, after char removal, unless otherwise specified as a "skimmed oil".

A cetane value engine test (ASTM D-613-79) was planned, but it proved impracticable to separate char and oil from the combined bulk product, since this was obtained before a method was found to achieve spontaneous char/oil separation. The combined product was deemed too viscous for the test, having apparently thickened during storage. However, in commercial practice, this product would be burned as a boiler fuel in a sewage treatment plant rather than used as a diesel oil. For diesel oil use, refining of the crude product will be needed.

Water and Ash Content, and Heating Values of Product Oils

Water contents of oils generated from sewage sludge are shown in Table 9, together with heat and ash contents and adjusted heat values.

TABLE 9: WATER, HEAT, AND ASH CONTENTS OF OIL PRODUCTS

Run #	Water (%)		Heat Value (cal/g)		Ash Content (%)		Adj. Heat Value (cal/g, ash-free)
	Measured	Ave.	Measured	Ave.	Measured	Ave.	
208(s)	ND	--	8741; 8912	8827	ND	--	--
208	7.94; 8.78	8.36	8940; 8001 8100	8347	8.1; 6.6	7.4	9909
305	9.37; 10.10	9.73	7835; 7768	7802	5.7; 5.7	5.7	9926
306	4.46; 5.85	5.16	8569; 8601	8585	6.3; 6.3	6.3	9696
313	7.68; 9.17	8.43	8716; 8667	8692	3.2; 3.5	3.4	9858
418	5.69; 5.39	5.54	8809; 8814	8812	0.93 0.65	0.47	8854
502-1	0.53; 0.33	0.43	8627; 8621	8624	ND	--	--
502-2	3.88; 3.06	3.47	8553; 8530	8542	5.7; 5.5	5.6	9436
502-3A	ND	--	8951; 8989	8970	3.7; 3.5	3.6	--
507-4	ND	--	8098; 8153	8176	2.3; 1.9	2.1	--
507-5	12.1; 12.1	12.1	8686; 8686	8686	14.7; 15.8	15.4	11984
507-6A	9.10; 8.70	8.90	8193; 8146	8170	3.4; 3.8	3.6	9337
509-6	ND	--	7674; 7681	7678	15.9; 16.6	16.3	--
509-7A	5.02; 5.10	5.06	8500; --	--	1.7; 1.7	1.7	9116
509-7B	ND	--	8487; 8491	8489	ND	--	--

ND - Not Determined

* Ash and water contents not determined on every sample. Values were determined after heating to 750°C for 8 hr.

+ - High ash contents in #507-5 and 509-6 may be due to char inclusion. Heat content determined according to ASTM-D-3286-77 throughout.

The heating values of oil products, determined by bomb calorimetry, were all very high. The overall average value was 8460 cal/g, with a range of 7678 to 8970 cal/g, on an as-recovered basis. The individual values are all too close together to indicate any effect of reaction conditions, and apparently the same product was obtained throughout. These values compare with n-octane (11,410 cal/g), being between 67.3 - 78.6% of the n-octane value, as recovered. On a dry, ash-free basis, for example, this translates to a value of 86.8% of n-octane for run 208 oil. Water content of the oils varied widely between less than 1% to over 12%, while ash content was between 2.1 to over 16%. These variations almost certainly represent differences in product homogeneity rather than bona fide changes due to reaction parameters.

Elemental Analysis

Organic elements (C, H, N, O) were determined in duplicate on a Perkin-Elmer elemental analyzer. Results are shown in Table 10, and are for as-extracted oils (including small amounts of ash and water).

TABLE 10: MAJOR ELEMENTAL COMPOSITION OF PRODUCT OILS

Run #:	C %	H %	N %	O %
208(s)	74.28, 74.30	10.99, 10.54	1.18, 0.81	ND
208(2)	75.77, 76.57	10.43, 10.07	2.02, 1.96	9.29, 9.31
305	71.47, 71.06	10.03, 9.50	5.10, 2.67	11.32, 10.33
306	69.51, 71.74	9.99, 9.84	2.45, 2.68	9.47, 9.38
313	73.31, 73.31	10.45, 10.03	2.82, 3.20	10.76, 11.11
418	74.83, 74.69	10.31, 10.08	3.36, 2.82	8.46, 8.96
502-1	78.57, 72.74	10.18, 10.62	1.78, 2.19	11.42, 11.21
502-2	73.07, 72.83	10.83, 11.00	2.85*	16.65, 15.95
502-3A	73.84, 74.68	10.36, 11.49	2.09, 2.80	12.37, 12.01
507-4	67.05, 67.85	10.41, 11.05	1.34, 2.05	12.43, 12.75
507-5	72.90, 73.29	10.76, 11.04	1.83, 1.84	ND
507-6A	72.11, 73.19	10.34, 9.92	1.99, 2.15	9.87, 9.60
509-6	72.32, 72.25	10.64, 10.05	2.02, 2.58	ND
509-7A	72.24, 71.04	10.89, 10.09	2.44, 0.77	9.03, 9.62
509-7B	73.94, 73.75	10.69, 10.19	2.94, 2.40	ND
Cellulose	41.87, 42.12	6.21, 6.23	-0-	45.51, 45.38
Cellulose, actual	44.44	6.22	-0-	49.34

ND = Not determined

* Single determination due to small sample.

Overall averages: C, 72.95%; H, 10.43%; N, 2.31%; O, 10.97%

Heavy metal, phosphorus and sulfur contents of oils were determined by X-ray fluorescence spectrometry. directly on the oil samples Summary results are shown in Table 11; complete data are given in Appendix B3.

TABLE 11: SUMMARIZED INORGANIC ELEMENTAL COMPOSITION OF PRODUCT OILS

Element (ppm): Run #:	Al	Si	P	S	Cl	K	Ca	Fe	Cu	Zn
208	1530	417	518	5870	656	15	163	561	48	108
305	2370	2060	960	8550	1860	181	1604	1966	112	183
306	2460	530	350	6270	22200	46	411	777	15	43
313	1530	410	550	5830	247	72	372	478	13	42
418	4650	280	510	9900	6380	39	85	782	7	59
502-1	1680	220	950	11140	285	116	53	352	6	17
502-2	1750	340	660	8790	6630	54	42	137	6	20
502-3A	2060	320	960	11950	563	9	22	79	4	5
507-4	2050	1330	690	8950	2330	129	41	135	4	11
507-5	1640	1770	770	10680	2700	82	41	321	4	6
507-6	2040	620	220	5710	35700	42	22	269	3	7
509-6	2860	260	750	9830	6980	65	25	114	7	12
509-7A	1950	2180	232	5450	18280	59	20	131	4	9
509-7B	1920	390	1000	11270	1024	8	45	58	1	13

Fractional distillation

A 250 ml sample of bulk oil was obtained by exhaustive methanol extraction of the bulk product from runs 208-313 containing char and water, followed by removal of most of the methanol under vacuum on a rotary evaporator. Considerable difficulty was encountered with sudden foaming during the evaporation, particularly towards the end when water was being removed. This difficulty continued when we attempted a vacuum fractional distillation. The following fractions were obtained without difficulty:

Fraction 1 - Clear white, 14 ml.
Fraction 2 - Cloudy white, 10 ml. (slight yellowing overnight).
Fraction 3 - Pale yellow aqueous (15 ml) under yellow oil (2.5 ml).
Fraction 4 - Same two phase product as #3, pot temperature increasing rapidly from 115 to 192°C., while distillation slowed (2 ml).

Fractions 1 and 2 were mostly methanol, while fractions 3 and 4 were mostly water with some light distillate. Gas chromatography/mass spectrometry analysis of these fractions was performed, but apart from methanol and water, the composition was too complex to permit identification of individual compounds.

The oil sample had been produced some 8-9 months prior to the experiment, had been stored in a mixed dichloromethane/water environment in 5 gallon drums at ambient temperatures outside, and then had been dewatered, had solvent removed, and extracted again with methanol to extract oil into solution and away from residual char. The resulting material was much different from a freshly prepared oil, being viscous and tarry. Presumably the combination of conditions resulted in continued increase in molecular weight during storage. Foaming made vacuum distillation impossible, and made careful control essential throughout the atmospheric distillation as well. There was some smoking during collection of fraction 3, and non-uniform bubbling during collection of #4. A further attempt at vacuum distillation was made on the cooled residual. At a temperature of 247°C under 34 mm Hg, the material appeared to decompose. The residual from this resembled a hard wax or plastic material rather than a coke, and consisted of 80% of the original material. This is all consistent with a polymerized product, and is in complete contrast to the results from our previous project (2) on conversion of sewage sludge to a synthetic asphalt material by liquefaction and fractional distillation. In this case, a freshly- prepared oil was vacuum distilled to yield a light oil and an asphalt. The light oil remained stable at room temperature after 3 years. The conclusion to be drawn from this is that the fresh product oil from future experiments should be decanted and either burned or fractionally vacuum distilled within a month of production, for best results. In light of this unanticipated result, there seemed to be no point in attempting to proceed with an engine test. This should be performed with a fresher sample. Additional work on oil aging under various storage conditions would also be very useful. The fact that mass spectrometric (GC/MS) analysis of distillate fractions of the 'old' oil derived from methanol extraction of the bulk product showed a highly complex result, an estimated 1000+ compounds being present, supports the hypothesis of continued reaction of oil components after production.

Differential Scanning Calorimetry and Thermogravimetry

Distillation characteristics of the product were determined by DSC and TG. Table 12 shows the temperatures for 50% loss of volatiles from the oils, together with the final residue percentage, in air and in nitrogen. The lower temperature for 50% weight loss in helium versus in air is attributed to the higher diffusion rate or organic molecules into a helium atmosphere, while the lower final readings encountered for the runs in air are likely due to actual combustion of the residual material.

The actual TG and DSC curves are presented in Appendix C. They vary between a continually increasing rate of volatile loss in inert gas due to distillation (e.g., run 208), to an almost constant rate of volatilization (e.g., runs 305, 306, 313, 502), to examples where there are significant discontinuities in volatilization rate (such as in runs 502-3A and 509-7B). The curves which were produced by heating oils in air have the same general shape as those obtained in nitrogen, but with 'humps' corresponding to oxidation of components. Examples of this latter case are runs 208 and 502-2 (Appendix C). The DSC results are useful to indicate whether a 'hump' is due to oxidation or to endothermic volatilization of a component, since the presence of a valley or a peak, respectively, on the appropriate chart provides

TABLE 12. VOLATILIZATION OF OIL BY THERMOGRAVIMETRY

Run #	50% Wt. loss temp in: Air	Helium	Residue at final temp. Air %	at °C	Helium %	at °C
208	320	250	14.24	530	10.63	530
305	420	400	25.55	520	25.13	520
306	310	290	2.80	620	11.32	590
313	400	380	8.19	620	10.98	620
418	390	310	4.00	630	19.00	620
502-1	410	360	7.37	620	16.95	620
502-2	350	270	4.60	620	12.20	620
502-3A	275	270	0.80	620	9.33	620
507-4	410	280	8.31	620	13.14	620
507-5	410	310	8.92	620	15.18	620
507-6A	360	290	3.04	620	12.64	620
509-6	350	280	4.03	620	12.21	620
509-7A	385	280	10.33	620	13.24	620
509-7B	290	260	0.40	620	10.50	620

a clear demonstration. Since DSC measures the rate of heat absorption or evolution rather than a cumulative loss in mass, it is sometimes easier to interpret than the equivalent TG result. However, DSC results with these oils are quite variable. For example, oil from run 313 shows a significant exotherm in air, beginning at 270°C and continuing to the end of the measurement at 390°C. This was not present in nitrogen, and is therefore due to oxidation. A similar result was obtained with oil from run 502-1. Other oils gave almost identical curves in air and in nitrogen, while that from run 507-4 has a series of endotherms from 70-150°C (perhaps due to loss of volatiles and water). Oil from 509-7A shows two sharp oxidation peaks at 350°C which were not present in the ostensibly identical sample from 7B. It is apparent from these results that, although general conclusions can be drawn on oil quality, there is still much to be learned about the variations in properties resulting from different production, extraction, and aging conditions. This fact is brought out even more emphatically by the fractional vacuum distillation results.

The TG results were far different from fractional distillation. For example, run 208 oil left only a 10.6% residue after heating to 530°C in helium, and only a 14.2% residue in air. This was an average result. Apparently the bulk oil had undergone some changes during storage outside for 6 months. The sample given as an example was 162 days old at the time of analysis. (The age of oils at the time of TG and DSC analysis can be derived from the difference between the run number (Run 208 for example was performed on 2-08-84, run number being the date), and the date on the TG or DSC chart in Appendix C. Where relevant, ages of oils at the time of analysis are included in the text).

Oil Viscosity

Attempts to determine viscosity of oils from runs 208-418 directly were unsuccessful; apparently the dichloromethane extraction process results in a more viscous product than is obtained by skimming the oil from the surface of the aqueous phase. This may be due to removal of the last traces of water from the oils, loss of volatiles during removal of the dichloromethane solvent from the extract, or an increase in molecular weight of the oil due to heating during extraction and solvent removal. Viscosities from runs 208-418 were all above 10000 cp (i.e., above the measurable limit with the apparatus) while viscosities determined on skimmed oils from runs 502-509 were generally below 1000 cp. Pour point data therefore substitutes for viscosity measurement for the earlier runs. There are three reasons why we believe the viscosities of oils from later runs are much lower than those from the first runs: Different reactor conditions, oil viscosities measured much earlier (the ages of the oils listed in Table 13 were all between 79-88 d at the time of viscosity measurement, while earlier runs were all above 100 days prior to analysis) and the presence of water in the oil. For the latter reason, results on samples 502-1, 507-5, and 509-7B are not included here, as they are probably highly aqueous.

Viscosities of oils from runs 502-509 are shown in Table 13, and were determined on a Brookfield viscometer using spindle numbers and speeds indicated, at 50°C after a 20 min equilibrium period. It was difficult to obtain constant readings, suggesting that these oils may have some non-Newtonian fluid properties.

Based on this viscosity data, the oils may be too unstable for use if stored for longer than 2 months (60 d), unless the increase in viscosity can be retarded by use of an antioxidant. However, use in a sludge treatment plant would be expected to be within the 60 d period. An alternative would be to perform a fractional distillation immediately after production, if foaming problems can be overcome.

TABLE 13. OIL VISCOSITIES

Run #:	Spindle #	Speed							
		0.3	0.6	1.5	3	6	12	30	60
502-2	18	240	190	160	165	127	94	63	42
502-3A	18	240	105	138	183	150	100	46	33
507-4	18	-	1438	1170	725	393	245	-	-
	34	-	-	-	-	-	55	50	45
507-6A	18	490	295	198	146	112	89	67	-
509-6	18	315	300	182	141	275	-	-	-
	34	-	500	320	280	230	245	292	305
509-7A	18	1350	990	796	774	-	-	-	-
	34	5200	3200	1960	1620	1400	1225	756	451

Pour point

1. Extracted oils - Approximately 5 g of oils from runs 208, 306, 502-3A, and 507-5 were heated in an oil bath. Product 502-3A became soft at 107°C and the other samples at 111°C, but none became pourable. Softening appeared to continue to 125°C, but at 130°C the oils became thicker. On continued heating to 155°C, the thickening continued, and on cooling to room temperature the originally soft products became hard, although still plastic. A repeat of this experiment with stirring (although ASTM D-97 does not permit stirring) gave identical results. Larger samples of extracted oils used for drying and ashing appeared to melt in the oven between 105-115°C.

2. Skimmed oils. Results of pour point tests according to ASTM D-97 (where oils are cooled to the lowest temperature which still permits flow) were as follows (Table 14):

TABLE 14. POUR POINT VALUES FOR SKIMMED OILS

Run #	Pour Point
502-3A	-2.7°C
509-6	-2.7°C
509-7A	-2.5°C

Flash Point

Corrected flash points of extracted oils according to ASTM D-97 were as follows (Table 15):

TABLE 15. FLASH POINT VALUES

Run #	Flash Point, °C.
208	182.3
305	179.6
306	168.4
313	174.1

CHAR CHARACTERIZATION

Yield, ash content, major element, and heavy metal analysis were determined for the product chars. One additional datum was obtained for each char - heat content - in addition to the above, to allow the calculation of approximate heat balances. The char burn test was carried out on the smaller scale alternative of the two alternatives outlined in the original proposal as there was insufficient material for a full-scale test. The following table (Table 16) provides the data obtained from char organic element, ash content, and heat value analysis. Table 17 gives data on the major inorganic elements present in chars. Additional data on minor inorganic components is presented in Appendix B3.

Char produced during these experiments yielded few surprises, in contrast to the results with some oil products. Liquefaction converted sludge with a heating value of about 3000 cal/g to a char with heating values ranging from 1100-3100 cal/g. Ash contents ranged from 43 to 80%. Yields of char were between 14-36% This variation is probably due to incomplete extraction of the oil from the char. In fact, the distinction between char and oil may be more of a continuum than a sharp difference: In experiments where oil and char did not separate from the water phase, this is believed to be due to oil absorption onto char, the average density of the combination being near to one.

Char Burn Test

The char sample for this test was obtained from ca. 1 l of combined product from runs #208, 305, 306, 313, following a 72 hr methanol extraction in a Soxhlet apparatus. The residue after this exhaustive extraction was designated as 'char'. It was black, and had a slight but offensive odor reminiscent of burned rubber. It was inert to a lighted match at room temperature, but ignited readily when heated over a gas flame. The flame was yellow and smoky, and gradually died out on removing the heat source. Re-application of the flame led to repeat ignition. This was repeated several times. The char became plastic when hot, and very tarry. Removal of the sample to a copper gauze (to allow air flow through the sample) and heating led to re-ignition, and smoldering combustion when all of the volatiles had been consumed. The bulk of the sample remained black after burning had ceased. The residue was then transferred to an oven and ashed at 750°C for 4 hr., leaving a light-colored ash. The composition of this ash is shown in Table 17.

Numerical results: Original char weight = 27.62 g.
Weight after burning = 16.84 g.
Weight after ashing = 10.02 g.

Hence, ash content of combined char was 36.28%, or, by difference, 63.72% organic material, of which 61% burned readily, and the remainder burned at 750°C. An analysis of the inorganic components of char ash is shown in Table 18.

TABLE 16. CHAR COMPOSITION

Run #	C %	H %	N %	O %	Ash %	Heat Value cal/g
208	30.88	3.82	1.26	9.74	58.6	2416
	31.94	3.57	1.57	9.99	59.4	2394
305	13.16	1.67	1.05	11.58	79.6	1178
	12.02	1.46	-0-	12.08	78.5	1194
306	13.51	1.64	-0-	16.36	78.7	1779
	12.69	1.55	-0-	16.45	77.5	1758
313	32.76	4.22	2.17	24.16	55.2	3150
	29.98	3.71	0.80	22.99	58.5	3185
418	26.62	3.67	0.17	22.42	50.20	2815
	27.49	3.66	0.33	21.08	50.11	2847
502-1	19.96	2.84	-0-	27.09	48.79	1817
	17.12	3.33	-0-	25.49	48.25	1789
502-2	16.78	3.17	-0-	27.28	44.98	1423
	16.10	3.48	-0-	26.41	45.14	--
502-3A	15.11	3.18	-0-	26.06	52.39	1462
	15.33	3.06	0.13	26.15	51.52	--
507-4	21.04	3.47	-0-	26.96	51.24	2026
	19.23	3.26	0.16	27.73	51.56	2058
507-5	21.48	3.55	0.03	24.75	55.65	2348
	22.04	3.59	0.21	22.46	55.99	2435
507-6A	29.05	4.30	-0-	22.69	47.85	3121
	27.98	4.22	-0-	23.31	47.59	3154
509-6	16.52	2.88	0.08	24.03	55.88	1702
	17.15	2.96	-0-	21.54	55.21	--
509-7B	24.47	0.36	0.86	22.35	42.60	2599
	24.65	3.56	0.80	22.91	44.44	--
Average	21.35	3.09	0.37	21.70	55.59	2148

+ -0- value was a measured result.

- Single heat values determined in some cases due to lack of sample.

$ There was insufficient sample for analysis of product from run 509-7A.

TABLE 17. CHAR ASH ANALYSIS

Source	Element	%	±	Source	Element	PPM	±
Ti	Al	1.80	0.19	Ag	U	23.0	2.7
	Si	10.25	0.54		Sr	311.	22.
	P	2.63	0.15		Y	10.9	1.3
	S	0.112	0.064		Zr	1780.	120.
	Cl	1.091	0.058		Nb	5.18	0.94
	K	0.649	0.034		Mo	245.	17.
	Ca	9.24	0.46		Th	13.0	2.6
		PPM	±				
Zr	V	<54.		Am	Ru	<5.0	
	Cr	941.	53.		Rh	<4.7	
	Mn	422.	27.		Pd	<4.0	
	Fe	4.46	0.22		Ag	97.6	7.4
	Ni	598.	31.		Cd	<5.7	
	Cu	812.	91.		In	<6.0	
	Zn	7970.	400.		Sn	263.	19.
	Ga	14.9	2.5		Sb	14.0	4.0
	Se	6.25	0.88		Te	<9.3	
	Pb	270.	14.		I	13.7	5.7
	As	<4.5			Cs	<11.	
	Br	13.2	1.0		Ba	1430.	100.
	Rb	17.2	1.2		La	38.4	9.6
					Ce	<18.	

TABLE 18. MAJOR INORGANIC ELEMENTS IN CHAR

Run #	208		305		306		313		418	
Element (%)		+/-		+/-		+/-		+/-		+/-
Al	2.60	0.18	2.93	0.21	3.02	0.27	1.35	0.13	0.59	0.095
Si	11.18	0.57	14.63	0.75	16.67	0.86	9.70	0.50	3.09	0.17
P	3.13	0.17	3.85	0.21	3.96	0.22	2.26	0.12	0.99	0.061
S	0.909	0.051	0.963	0.055	0.838	0.054	1.057	0.057	0.526	0.031
Cl	0.069	0.000	0.059	0.009	0.040	0.011	0.084	0.008	0.135	0.009
K	0.307	0.016	0.520	0.027	0.561	0.030	0.309	0.016	0.222	0.012
Ca	7.78	0.39	11.47	0.57	11.52	0.58	7.81	0.39	2.77	0.14
Ti	0.526	0.027	0.544	0.028	0.381	0.021	0.331	0.017	0.151	0.008
Fe	3.24	0.16	5.58	0.28	4.64	0.23	3.34	0.17	1.14	0.057

Throughout this test, the char combustion was reminiscent of the behavior of powdered coal, with the exception of the tarring. We concluded that the char would be an acceptable fuel source, although problems could develop because of the high ash content and relatively low heat value, and the high temperature required for complete combustion. Further study of char burning needs to be done before this product can be used as a fuel source for the reactor.

The combustion test with a char sample showed that it will burn, and so can be used as a source of fuel for the liquefaction reactor. Heavy metals in the sludge were concentrated in the char, as expected. The oxygen content was quite high (ca. 45%), which explains the relatively low heating value compared to oil. In practice, since the char and oil would be used to provide fuel in a water treatment plant, to run the reactor and dewatering equipment, they would probably be recombined after separation from the wastewater. A discussion of the relative yields of char and oil as a function of reaction conditions is therefore unnecessary.

PRODUCT YIELDS AND PRODUCTION CONDITIONS

Weight yields of oils and chars extracted from the dichloromethane-extracted analytical samples prepared as described previously are given in Table 19.

TABLE 19: PRODUCT YIELDS AND PRODUCTION CONDITIONS

Run #	Conditions*: (°C)	(min)	(psi)	% Feed solids	Weight (in g) of: Sample	Char	Oil	Yield (in %) of: Char	Oil
208	305	90	1700	20.7	233.85	11.45	4.95	23.65	10.23
305	275	180	1700	23.6	215.83	5.75	10.28	11.29	20.18
306	305	180	1750	18.8	190.53	5.40	8.92	15.08	24.90
313	275	90	1750	19.8	221.63	5.27	7.42	12.01	16.91
418	275	90	2000	20.2	237.46	11.59	8.46	24.14	17.62
502-1	275	105	2150	20.2	232.46	2.67	4.62	5.68	9.83
502-2	275	114	2150	20.2	236.61	2.00	7.51	4.18	15.71
502-3A	275	200	2150	20.6	260.56	3.17	4.78	5.91	8.91
507-4	275	165	1650	20.7	250.66	2.41	8.99	4.65	17.35
507-5	275	152	1250	20.7	211.92	12.69	8.60	28.97	19.63
507-6A	275	261	2150	20.7	241.06	8.08	18.09	16.22	36.30
509-6	275	252	2050	19.4	175.84	1.64	4.78	4.81	14.01
509-7A	275	57	2050	19.4	190.34	--	6.25	--	16.90
509-7B	275	60	2060	19.4	230.61	1.66	3.18	3.70	7.10

* Nominal conditions for temperature, pressure and residence time; actual values vary somewhat - see reaction profiles (Appendices A1-A8).

+ Yields calculated from feed solids content, on a dry weight basis.

DATA REDUCTION

Results obtained by analysis of oil, char, wastewater, and gas products have been discussed in the context of the reactor conditions used for production, and the overall goals of the project. In the following section, data obtained by various methods are correlated, reduced, and compared to give a presentation of the efficiency of continuous sludge liquefaction. This will serve as a basis for discussion of the results and for the economic analysis which follows.

The major numerical items of interest for the following discussion are product yields in terms of mass and energy, to answer the question whether continuous liquefaction works, and if so, if it converts sludge efficiently. In Table 20, empirical data presented elsewhere in this report are assembled and mass and energy yield calculations performed. Bearing in mind that the theoretical oil and char mass yield from sewage sludge is between 60-70% of the starting material weight (due to loss of water and carbon dioxide from the feed during liquefaction chemistry), actual yields varied between 18-70% based on organic material. At the same time, energy yields varied between 22-79% (ignoring one result over 100%). The process did in fact work, based on these results, and under certain conditions did so efficiently.

The simple arithmetic given in Table 20 represents the major portion of data reduction for this project. The following example calculation of mass and energy yields of oil and char from Run 306 is provided to facilitate interpretation of Table 19 and Table 20:

Sample Yield Calculation: (sample containing Na_2CO_3)

Feed sample weight = 190.53 g; Solids content = 18.84%;
Original weight of feed in sample = 190.53 x 18.84/100
= 35.90 g;

Weight of char extracted = 5.40 g
Weight of oil extracted = 8.92 g

Hence, weight yield of char = (5.40 x 100)/35.90 = 15.04%
and, weight yield of oil = (8.92 x 100)/35.90 = 24.85%
(includes ash);

Ash content of dry feed = 35.67%, so organic content = 64.33%
Weight of organics in dry feed = 35.90 x 0.6433, = 23.09 g

Ash content of char = 78.10%, of oil = 6.3%. By a similar calculation,

Ash-free weight of char = 1.18 g; of oil = 8.36 g

Hence, weight yield of char = (1.18 x 100)/23.09, = 5.11%
weight yield of oil = (8.36 x 100)/23.09, = 36.21%
And, total oil + char organic yield = 41.32%;

Heat content of feed = Weight of feed x unit heat value (g)
= 35.90 g x 3290 cal/g
= 118,111 cal

Similarly, heat content of char = 5.40 g x 1768 cal/g
= 9,547 cal
heat content of oil = 8.92 g x 8585 cal/g
= 76,578 cal

Therefore, energy yield in char = (9,547 x 100)/118,111, = 8.08%
energy yield in oil = (76,578 x 100)/118,111 = 64.84%

Total energy yield in oil and char = 8.08 + 64.84 = 72.92%

A total of 8 continuous runs was performed during this project, including 5 full-length runs and 3 runs where conditions were changed during the run. In our original concept, steady state conditions would have been achieved during each run, whereupon a sample of product would be taken. For the set of conditions initially proposed, there would have been 9 runs (3 runs at 250, 300, and 350°C and at 3 residence times of 0.5, 1.5, and 3 hr at each temperature) based on a residence time definition of one-third of the total reactor volume. The objective was to find a set of conditions where above a 60% energy recovery in product oil and char was achieved. In practice this was achieved with run #306 and again with run 418, and was closely approached on run 305 (58% energy recovery). Rather than trying to improve yields in subsequent runs, we decided to concentrate on improving product separation, as this had been poor or nonexistent in the first experiments, and good product separation from wastewater was considered vital to the future development of the process. The remaining runs were therefore designed to test the effect of pressure on product separation rather than to maximize yield. Most of the work was performed within a fairly narrow temperature range of 275-305°C, with residence times in the whole reactor volume of 1.5 to 3 hr. Longer residence times would have been practicable, although shorter times would have exceeded the capacity of the metering pump and the cooling system.

The first result of note was that below 250°C there was no noticeable reaction of the sludge; a preliminary run at 250°C yielded no oil although the solids had been digested in the alkaline medium. Above 265°C a rapid endothermic reaction set in, temporarily exceeding the capacity of the heaters. At 275°C, where all but two of the runs were performed, feed conversion to products was total. Beyond this point a discussion of relative efficiencies of conversion at 275 or 300°C and 1.5 or 3 hr residence time is of questionable value, as each yield is based upon a single experiment. In the last 3 runs, steady state conditions probably were not achieved because of mixing inside the reactor. From the data obtained, it made little difference to product yields whether the reaction was run at a low or high temperature or for 1.5 or 3 hr. This indicates that the conversion of sludge to oil occurred in less than the lowest residence time (i.e., in less than 1.5 hr).

According to results obtained using autoclaves, a 3 hr residence time in the reactor was considered to be the minimum to obtain liquefaction and oil/char formation, at 320°C. The reactor was designed around these parameters.

It was quickly learned that complete reaction occurred at the lowest practical residence time and within a few degrees of the temperature where the reaction started (265°C.) This is an excellent result in terms of design and process economics, because of the facts that equipment can be run at lower temperatures, pressures, and residence times than previously thought possible, with corresponding decreases in the power, thickness, and size of the equipment.

It is important to distinguish between the processes of sludge dissolution to soluble materials, oil and char formation through continued reaction of water-soluble materials, and product separation from water after reaction and cooling. From examination of the temperature/pressure profiles during a run, it was apparent that within 10-15 min of the feedstock reaching 265°C, the endotherm for the reaction was overcome by the heaters and temperatures inside the reactor recommenced rising. This is believed to correspond to the sludge dissolution and degradation phase, forming water-soluble, low molecular weight products through hydrolytic reactions. After this, these products recombined through Aldol reactions, condensations, cyclizations, and related reactions to form oil (water-insoluble) products, and eventually char and high molecular weight tars. (This process has been extensively investigated by us using a range of feedstocks, in the laboratory). Following this, the products exit from the reactor through the let-down process into the collection drum, where spontaneous separation of water, char and oil phases occurs. In several of the earlier runs, such separation either did not occur, or was very slow.

In considering the possible reasons for this, we thought of two possibilities: Incomplete reaction, with a large proportion of residual water-soluble compounds, or emulsification caused by too rapid mixing as a result of gas bubble formation. Chemical analysis of the products eliminated the first possibility. Raising the gas overpressure, it was felt, would relieve the second problem by preventing local boiling, although it would not affect gas formation through liquefaction reactions. In fact, an increased nitrogen overpressure in runs 418 and 502-509 resulted in rapid product separation from wastewater, spontaneously, within a day. The separation was good (the water phase was transparent, although light brown), but further work needs to be done on the actual combination of conditions leading to best separation as well as to the best and most rapid liquefaction. These conditions may not be identical. Also, since oils from the first runs were isolated through solvent extraction, it was felt best to continue doing this to maintain continuity of analysis. By visual observation and viscosity and pour point measurements it was apparent that oils obtained in the high-overpressure runs by spontaneous separation, decantation, and drying were superior to those obtained at lower pressure, through extraction. Whether this is due to reaction conditions or continued reaction of the products during the dewatering/solvent extraction is not clear. We have previously noted a rapid viscosity increase in oils heated above 100°C, which is apparently not due to water loss, and which could explain the high viscosity of the extracted oils. Alternatively, retention of water in the decanted products could also explain their relatively low viscosity. Further work with decanted oils would resolve this question.

TABLE 20. MASS/ENERGY YIELDS OF OIL AND CHAR PRODUCTS

Run #:	208	305	306	313	418	502-1	502-2	502-3A	507-4	507-5	507-6A	509-6	509-7A	509-7B
Sample wt.	233.85	215.83	190.53	221.63	237.46	232.46	236.61	260.56	250.66	211.92	241.06	175.84	190.34	230.61
wt. char	11.45	5.75	5.40	5.27	11.59	2.67	2.00	3.17	2.41	12.69	8.08	1.64	-0-	1.66
wt. oil	4.95	10.28	8.92	7.42	8.46	4.62	7.51	4.78	8.99	8.60	18.09	4.78	6.25	3.18
% Feed solids	20.73	23.58	18.84	19.78	20.22	20.21	20.21	20.59	20.18	20.18	20.67	19.40	19.40	19.40
wt. Feed solids	48.48	50.89	35.90	43.84	48.01	46.98	47.82	53.65	50.58	42.77	49.83	34.11	36.93	44.74
% Feed Organics	65.26	66.07	64.33	65.37	65.92	62.26	62.26	61.33	62.81	62.81	62.81	65.19	65.19	65.19
Wt. Feed organics	31.64	33.62	23.09	28.66	31.65	29.25	29.77	32.90	31.77	26.86	31.30	22.24	24.07	29.17
Wt. yield char**	23.62	11.30	15.04	12.02	24.14	5.68	4.18	5.91	4.76	29.67	16.22	4.81	-0-	3.71
Wt. yield oil**	10.21	20.20	24.85	16.93	17.62	9.83	15.70	8.91	17.77	20.11	36.30	14.01	16.92	7.11
Ash content char (%)	59.00	79.05	78.10	56.85	50.16	48.52	45.06	51.96	51.40	55.82	47.72	55.55	--	43.52
Ash content oil (%)	7.4	5.7	6.3	3.4	0.47	ND	5.6	3.6	2.1	15.4	3.6	16.3	1.7	ND
Wt. char organics	4.69	1.20	1.18	2.27	5.78	1.37	1.10	1.52	1.20	5.61	3.93	0.73	-0-	0.94
Wt. oil organics	4.58	9.69	8.36	7.17	8.42	--	7.09	4.61	8.80	7.28	17.44	4.00	6.14	***[+]
Organic char yield (%)[+]	14.82	3.57	5.11	7.92	18.26	4.68	3.69	4.62	3.78	20.89	12.56	3.28	-0-	3.22
Organic oil yield (%)	14.48	28.82	36.21	25.02	26.60	--	23.82	14.01	27.70	27.10	55.72	17.99	25.51	***
Combined organic yield	29.30	32.39	41.32	32.94	44.86	--	27.51	18.63	31.48	47.99	68.28	21.27	25.51	***
Heat content feed	3189	2952	3290	3325	3256	2938	2938	2869	3109	3109	2946	3180	3180	3180
Heat content char	2405	1186	1768	3168	2833	1803	1423	1462	2042	2392	3138	1702	--	2599
Heat content oil	8347	7802	8585	8692	8812	8624	8542	8970	8176	8686	8170	7678	8500	8489
Energy yield char	17.81	4.54	8.08	11.45	20.93	3.49	2.03	3.01	3.13	22.83	17.27	2.57	-0-	3.03
Energy yield oil	26.73	53.39	64.84	44.24	47.69	28.87	45.66	27.86	46.74	56.18	100.7	33.84	45.21	18.97
Total energy yield[+]	44.54	57.93	72.92	55.69	68.62	32.36	47.69	30.87	49.87	79.01	117.97	36.41	45.24	22.00

* Assumes H_2O constant.

[+] Includes ash

Ash-free

Excludes organics in gas and wastewater.

LIQUEFACTION CHEMISTRY

Table 21 shows overall average feed and product compositions taken from the experimental data together with ash contents both experimentally determined and by difference. The results are internally consistent, within experimental error limits.

TABLE 21. FEED/PRODUCT AVERAGE ELEMENTAL AND ASH CONTENTS

Material	C %	H %	N %	O %	Ash,% By Expt.	 By Diff.
Sludge	31.51	4.68	1.24	27.05	35.52	35.52
Oil	72.95	10.43	2.31	10.97	6.46 4.38*	3.34
Char	21.35	3.09	0.37	21.70	55.57	53.49

* Value with two highest (anomalous) results not included.

Table 22 shows the same average values on an organic basis, after correction for ash content:

TABLE 22. FEED/PRODUCT AVERAGE ORGANIC ELEMENT CONTENTS

Material	C %	H %	N %	O %
Sludge	48.87	7.26	1.92	41.95
Oil	75.47	10.79	2.39	11.35
Char	45.90	6.64	0.80	46.66

(Value of ash determined by difference used in calculation).

Elemental ratios determined by division by appropriate atomic weights are shown in Table 23:

TABLE 23. FEED/PRODUCT ORGANIC ELEMENT RATIOS

Material	C	H	N	O
Sludge	4.07	7.20	0.14	2.62
Oil	6.28	10.70	0.17	0.71
Char	3.82	6.59	0.057	2.92

Representing sludge values as unity, the ratios of major organic elements in oil and char products to feedstock are obtained in Table 24.

TABLE 24. RATIOS OF C,H,N,O IN PRODUCTS (FEED AS UNITY)

Material	C	H	N	O
Oil	1.54	1.49	1.21	0.27
Char	0.94	0.92	0.41	1.11

Differences in composition between the oil and char products are readily apparent. Carbon, hydrogen and nitrogen contents are all increased in the oil relative to the feed, while oxygen is significantly reduced (by a factor of approximately 4). In the char, excepting nitrogen content, all of the other elements are present in similar amounts to the values in the feed. This raises the possibility that the char does in fact represent unreacted feedstock rather than polymerized oil.

Using the ratios calculated above, it is possible to represent the conversion of sludge to products in the form of an equation:

$$\text{Sludge} \longrightarrow \text{Oil} + \text{Char (neglecting wastewater and gas)}$$

Dividing by the lowest value in Table 24 (above) gives the elemental ratios in numbers of unity or above (N = 0.057 becomes N= 1.0). Rounding off to the nearest whole number gives the net chemical change as:

$$C_{71}H_{126}N_2O_{46} \longrightarrow C_{110}H_{188}N_3O_{13} + C_{67}H_{115}NO_{51}$$

From Table 19, the average ratio of oil/char yields on an organic basis is 1:3.54. Using this ratio and combining oil and char as one product gives the modified equation:

$$C_{71}H_{126}N_2O_{46} \longrightarrow C_{101}H_{172}N_{2.5}O_{21}$$

Assuming a 100% recovery of carbon in oil and char, the theoretical yield of oil and char from sludge becomes

$$C_{101}H_{179}N_3O_{65} \longrightarrow C_{101}H_{172}N_3O_{21}$$

which calculates out to a value of 71%. Actually, of course, most of the oxygen is lost as carbon dioxide, and so carbon cannot be assumed constant. If the above equation is modified to reflect loss of water and carbon dioxide as follows:

$$C_{101}H_{179}N_3O_{65} \longrightarrow C_{81}H_{171}N_3O_{21} + 20\ CO_2 + 4H_2O,$$

which represents the actual experimentally determined change quite accurately, then the theoretical yield becomes 1523.2 ('molecular weight' of product)/ 2475.5 ('molecular weight' of feedstock), or 61.5%. The highest combined organic yield obtained experimentally (excluding run 507-6A, which may be anomalous) was 48% from run 507-5. A conversion of sludge to recoverable products of 48/61.5, or 78% of theoretical was obtained, therefore, the remainder being lost in the form of aqueous organic soluble compounds.

Changes in Inorganic Element Distribution During Liquefaction

Because the liquefaction process is an alkaline digestion, it has the potential for extensive degradation of toxic organic materials which may be present in the feed; preliminary laboratory work has demonstrated this for chloroform, lindane, and a 2,4,5-T analog (2,4,5-trichlorophenylpropionic acid). Also, hydroxides of most heavy metals are insoluble, and so should be precipitated from solution in the water portion of the feed during the liquefaction, providing a method for cleaning the wastewater of high levels of some toxic ions. This principle was borne out in practice, as shown by the data in Table 25, where selected inorganic element concentrations from 3 runs are compared between sludge feed, char and oil products.

TABLE 25. SELECTED INORGANIC ELEMENTS IN FEED AND PRODUCTS

Material:	Sludge			Char		Oil		
Run #:	306	418	502-1	306	418	306	418	502-1
Element:								
Cr	541	103.1	97.6	1107	220	19.5	13.9	11.7
Ni	20.1	27.9	26.9	308	73.1	9.3	9.6	8.0
Cu	309	339	302	2100	785	15.3	6.6	6.3
Zn	616	651	662	2500	1347	43.6	59.0	17.3
Pb	58.8	53.7	52.4	322	157	2.0	0.9	2.1
Ag	29.6	28.7	18.1	165	70.2	3.5	4.2	2.2
Cd	3.2	5.0	2.8	15.2	7.0	3.6	4.7	2.3
Sr	66.9	78.5	52.7	229	130	9.0	37.3	27.2
Sb	4.8	6.9	4.3	11.2	11.0	5.3	5.5	3.1
Te	5.1	8.3	4.8	4.4	14.0	5.7	6.9	3.3
Ba	369	319	309	1900	520	14.1	13.1	5.7

* Typical data taken from Run 306, 418, and 502-1 results.
+ X-ray analysis not done on char from run 502-1.

As expected, concentration effects depend to some extent on the solubility product for the element hydroxide in question. Chromium was concentrated about twofold in the char, zinc 2-4 fold, and lead 3-6 fold. Cadmium levels were too low in the feed sludge to permit any estimate of concentration effects in char, and mercury was subject to interference with germanium in the X-ray analysis and so was not reported. However, the trend is clear, and represents a useful bonus of the liquefaction process in removing heavy metals from water passing through the process. Assuming that most of the metal content in the oils is due to particles of ash and char carried through the extraction, it would be worthwhile to perform further research on liquefaction of sludges heavily contaminated with toxic heavy metals. By "spiking" a sludge with a known amount of a specific metal ion, such as cadmium, we could determine the resulting distribution of cadmium in the products. The experiment would also provide much needed data on residence times and distributions inside the reactor.

GAS ANALYSIS

Table 26 lists gas analysis results obtained. The absence of hydrogen in gas samples obtained after 3-06-84 is puzzling, and we have no explanation for it. There was no known change of procedure which could account for this anomaly.

TABLE 26. REACTOR OFF-GAS COMPOSITION

Run #:	Gas: Hydrogen	Carbon dioxide	Ethylene	Ethane	Oxygen	Nitrogen	Methane
1122*	1.58	9.50	0.15	0.24	0.69	87.72	0.12
	(13.63)+	(81.97)	(1.29)	(2.07)	-	-	(1.04)
1122	0.98	9.49	0.12	0.20	0.07	89.03	0.12
	(8.98)	(86.98)	(1.10)	(1.83)	-	-	(1.10)
208	4.75	39.4	0.24	0.22	0.06	54.52	0.80
	(10.45)	(86.74)	(0.53)	(0.48)	-	-	(1.76)
305	1.38	5.19	0.16	0.15	2.05	91.02	0.05
	(19.94)	(75.05)	(2.30)	(2.23)	-	-	(0.69)
306	1.40	6.52	0.13	0.13	1.66	90.13	0.05
	(17.03)	(79.62)	(1.53)	(1.59)	-	-	(0.56)
313	ND	3.63	0.05	ND	1.26	95.05	0.03
	(-0-)	(98.26)	(1.33)	(-0-)	-	-	(0.68)
418	ND	7.41	0.03	ND	0.03	91.68	0.02
	(-0-)	(98.40)	(0.33)	(-0-)	-	-	(0.31)
502	ND	1.95	0.04	ND	0.94	96.05	0.05
	(-0-)	(98.40)	(0.33)	(-0-)	-	-	(2.20)
507	ND	3.83	0.05	ND	2.05	94.79	ND
	(-0-)	(97.50)	(1.15)	(-0-)	-	-	(-0-)
509	ND	1.83	0.10	0.10	0.07	96.34	ND
	(-0-)	(90.40)	(4.70)	(4.90)	-	-	(-0-)

* Richland primary sewage sludge + peat moss

+ Normalized values, minus oxygen and nitrogen from air and purge gas, given in parenthesis. In run 208, carbon monoxide was also noted at 0.04% (0.08% normalized), and also in Run 418 (0.04%, 0.57% normalized). ND = not detectable.

A typical gas production rate was back-calculated as a percentage of feed carbon, according to the calculation shown for Run 306 below. Gas production accounted for 13% of carbon input principally as carbon dioxide. Variation in this was not significant enough to warrant a separate calculation of mass for each sample. Instead, a fixed value of 13% was used in calculating balances.

Storage tank pressure at 9:00 = 39.3 psi (2.67 atm)
at 9:15 = 59.0 psi (4.01 atm)
Volume of storage tank = 504 l
Gas produced in 15 min = (4.01 - 2.67) x 504 l at 17°C, = 675.36 l
Volume of gas produced per hr at STP = 2543 l
Gas composition = 90% nitrogen, 8% carbon dioxide, 2% hydrogen
Gas actually produced = 0.1 x 2543 l (excluding nitrogen), = 254.3 l
Average molecular weight of carbon dioxide/nitrogen mixture = 35.60

Gram-moles/hr of gas produced = 11.35,
= 404.2 g/hr
At 20% solids, 3 hr residence time, sludge solids input
= 46.5/5 x 1/3 kg/hr, = 3.10 kg/hr solids
Average carbon content of sludge solids = 34.50%
Average carbon content of gas = 33.74%
Carbon input in feed = 1069.5 g/hr
Carbon output in gas = 136.4 g/hr

Hence, % carbon in gas as a function of feed = 12.75%

The major component of the by-product gas was carbon dioxide, excluding the nitrogen used for pressure regulation. In practice, the gas produced in liquefaction would be used for pressure control. Some hydrogen was also generated in the early stages of a run, but in quantities insufficient to be significant. Entrapped oil and mineral particles and volatile organic compounds were also collected in the 'dogleg' portion of the let-down system and the gas storage tank, and would need to be collected and recycled to the product storage vessel. This would also be essential for environmental reasons, due to the obnoxious odor of the gas. After this was done, the gas could be vented to atmosphere without adverse effect on the environment.

WASTEWATER CHARACTERIZATION

Analysis of the wastewater from the liquefaction runs was to include BOD, COD, suspended solids, evaporation residue, pH, and dichloromethane extraction on selected samples, rather than on samples from every run. Techniques of analysis have already been described in the Materials and Methods Section. Results of these analyses are shown below:

TABLE 27. WASTEWATER ANALYSIS

Run#	Conditions (°C/hr.)	pH: Crude	pH: Filtered	pH: Extracted	Solvent soluble	Suspended solids	Evaporation residue
305	275/3	8.10	8.18	8.60	1.7*	0.19	--+
		8.11	8.12	8.62	1.9	0.20	87.6
313	275/1.5	8.40	8.40	8.70	1.7	0.20	81.3
		8.39	8.40	8.72	1.7	0.22	77.5
502-2	275/1.5	8.40	8.36	8.62	1.3	0.11	74.8
		8.39	8.40	8.73	1.4	0.05	85.1
							67.1

* Grams/liter
+ Sample bumped and was lost.

Results of COD and BOD analyses are shown in Table 28. Biodegradability of organic material in wastewater was determined as the ratio of BOD:COD expressed as a percentage (Table 29).

TABLE 28. COD AND BOD OF WASTEWATER

Run #	COD		Trial # BOD					
	1	2	1	2	3	4	5	6
305	50.6	54.6	38.56	40.08	38.64	40.92	40.68	42.12
313	61.2	62.4	39.44	38.32	37.28	41.04	34.44	36.72
502-2	39.8	41.9	29.60	28.24	27.44	26.64	26.52	27.96
Gl-Ga				243.5	260.0	260.5		

Values in g/l except for the glucose/glutamine standard (Gl-Ga), which is in mg/l.

Aqueous evaporation residue (dissolved solids), and ash contents were determined for runs 418 and 502-509 to enable us to better determine mineral balance and overall mass distribution during liquefaction. These results are reported in Table 30.

TABLE 29. WASTEWATER BIODEGRADABILITY

Run #	Run conditions	Av. COD	Av. BOD	S.D.*	% Biodeg.+
305	275/3 hr.	52.6	40.17	2.02	76.4%
313	275/1.5 hr.	61.8	37.87	2.09	61.3
502-2	275/1.5 hr.	40.8	27.73	1.04	68.0

* S.D. = standard deviation (+/-)
+ Percent biodegradability = BOD x 100/COD

TABLE 30. DISSOLVED SOLIDS ASH CONTENT

Run #	Solids (g/1)	Ash, % 1	2	Average	Organics, % (average)
418	77.8	57.42	57.25	57.34	42.64
502-1	79.7	61.95	62.40	62.18	37.82
502-2	67.1	66.96	67.12	67.04	32.96
502-3A	65.5	64.69	65.35	65.02	34.98
507-4	77.0	59.03	59.45	59.24	40.76
507-5	87.3	60.12	60.31	60.22	39.78
507-6A	71.6	57.87	58.09	57.98	42.02
509-6	75.1	62.36	-	-	37.64
509-7B	73.7	53.79	-	-	46.21

There was insufficient sample for an ash or residue determination on sample 7A. Organic content is by difference.

Anaerobic Digestion

The results of this test were negative. One of the two controls evolved 3.7 ml of gas while the others did not produce any, even after 8 weeks at 37°C. Adaptation of organisms to the largely phenolic and non-acidogenic organic compounds present in these wastewaters would probably be required to obtain a positive result.

Wastewater Treatability

At the beginning of this project, one of the main concerns was the question of wastewater treatability. This concern has been dispelled by the results obtained. Although COD was very high, the aerobic oxidation rate by a standard bacterial culture was also very high, corresponding approximately to that of glucose. Anaerobic digestion results were less encouraging, which is to be expected in the light of the organic water-soluble products from liquefaction: These are mostly phenols and low-molecular weight alicyclic and aliphatic compounds, more suitable to attack by aerobic than anaerobic organisms. From the results, we conclude that there should be no problem in recycling the wastewater from a liquefaction unit back through with the primary sludge input into the plant. The additional loading will be negligible.

The recycle liquor from the STOR process will result in additional indirect costs for the sewage treatment plant. These costs are included in Table 35 in the economics section of the report.

SECTION 6

LIQUEFACTION PROCESS PRELIMINARY ECONOMICS

INTRODUCTION

A preliminary economic evaluation of the sludge-to-oil process is developed for small towns of 10,000 people, medium cities of 100,000 people and large metropolitan areas of 1,000,000 people. The first part of this chapter describes the basis for the cost estimate. The second part describes the material, component and labor costs. The third part examines alternate sludge disposal costs and compares them to the estimated costs of the sludge-to-oil system.

ESTIMATE BASIS

The bases of the analysis are shown in Table 31. Sludge production is generally on the order of 0.07 to 0.11 kilograms per capita per day. A sludge production value of 0.08 kilograms per capita per day (dry basis) is used to estimate the sludge production. It is assumed that the baseline sludge consists of 65% organic material and 35% inorganic material. The wet sludge, when mixed with 5% Na_2CO_3, would be 25% solids. It would have a density of ca. 1.1 and occupy a volume of 3.82, 38.2 and 382 m^3. The sludge input to each size sludge-to-oil system would therefore be 76.2% water, 12.4% organics and 11.4% inorganics. At this point, the similarities between the three sizes ends. Due to the differences in size, the basic design of each plant is quite different.

Design Basis for a Town of 10,000

Heating 4.2 tonnes per day of the 25% solids reactor feed to 300°C requires 1.26×10^6 calories or 61 Kw (210,000 Btu/hour). In one year this plant would use 535,000 KwH (1.8×10^9 Btu). If the energy were supplied by electricity at a cost of $0.05 per KwH this amounts to $27,000 per year. If the energy were supplied by natural gas at $4.5 per 10^6 Btu, the annual cost would be $8,200. This demonstrates that heat recovery equipment would have to be quite inexpensive to be justifiable in a plant this small. One possible system would be to jacket the high temperature portion of the cooler and the preheater before the reactor. This jacket would then be filled with water and kept at a pressure where the water would boil in the cooler and condense in the preheater. This would require a little extra piping and a good pump, but would probably not add more than $10,000 to the cost. This heat recovery system would likely recover 50% of the heat input. Based on this heat

TABLE 31. ESTIMATE BASES FOR THREE STORS SIZES

Design Item	Small Town Pop. 10,000	City Pop. 100,000	Metropolis Pop. 1,000,000
Sludge Production* (Dry basis)	0.8	8.0	80
Sludge Organics (Dry basis)	0.5	5.0	50
Wet Sludge (20% Solids)	4.0	40	400
Sodium Carbonate Added	0.2	2.0	20
Reactor Feed	4.2	42	420
Oil Product	0.2	2.0	20
Char	0.12	1.2	12
Process Wastewater	3.2	32	320
Solids in Gas and Wastewater	0.68	6.8	68

* All units are tonnes/day.

recovery scheme we assume that a net temperature rise of 150°C would be supplied by the primary heater. For a small facility such as this, the product oil could probably not be used to fuel the process. Thus, the product would have to be incinerated on the site or transported away. This adds to the overall cost and does not allow the energy value of the oil to be considered a revenue.

Material and Component Costs for a Small Town

The material and component costs assume a 30 min residence time in the reactor high temperature zone. The volumetric flow rate of the sludge is about 3.82 m^3/d or 0.002652 m^3/min. In 30 min, this is equal to an accumulated volume of 0.0796 m^3. The reactor pipe size used for the process development unit, 6" schedule XXS pipe, has a volume of 0.012152 m^3/m of length. If this pipe were used for an 0.8 dry tonne per day facility, 6.55 m of pipe would be required for the high temperature zone. When this is added to an equal amount of pipe for the preheating zone of the reactor, the length of pipe needed for the whole reactor amounts to 13.1 m. This could best be assembled into two 6.55 m long segments. The pipe alone would weigh 1.05 tonnes. At a rough cost of $7/kg for chrome-moly steel, this amounts to $7,350 for the pipe.

Design Basis for a Medium City of 100,000

In a medium sized city the energy flows are large enough to warrant the use of heat recovery. A fairly detailed and proprietary design has been developed for a city of this size. In this design, a Dowtherm boiler is fired with the oil produced from the sludge. Vaporized Dowtherm is used as the heat transfer fluid to the high temperature portion of the reactor. Boiling and condensing water in the jacketed cooling and preheating sections would be used to recover heat. About 50% of the heat could be recovered in this manner. This size plant is too small to consider a high pressure steam boiler as the main heat transfer system.

Materials and Component Costs for a Medium City

The material and component costs assume a 30 min residence time in the reactor high temperature zone. The volumetric flow rate of the sludge is about 38.2 m^3/d or 0.02652 m^3/min. In 30 min, this is equal to an accumulated volume of 0.7958 m^3. The reactor pipe size used for the process development unit, 6" schedule XXS pipe, has a volume of 0.012152 m^3/m of length. If this pipe were used for an 8 dry tonne per day facility, 65.5 m of pipe would be required for the high temperature zone. When this is added to an equal amount of pipe for the preheating zone of the reactor, the length of pipe needed for the whole reactor amounts to 131 m. This could best be assembled into twelve 11 m long segments. The pipe alone would weigh 10.5 tonnes. At a rough cost of $7/kg, this amounts to $73,500 for the pipe.

If 61 cm (24" schedule 160) pipe were used, (0.189 m^3/m) about 4.2 m of pipe would be required for the high temperature zone. The entire reactor would require only 1 segment about 9 m long. This would weigh about 7 tonnes and cost about $49,000. The higher cost of the larger fittings would be offset by the smaller number required. In addition, the savings on the number of seals and motors for the scraper system would be large. However, heat transfer would be more difficult. Clearly, the selection of the reactor diameter is an important consideration in the actual design phase. This cost analysis uses the 61 cm (24") diameter pipe as the reactor vessel.

Another important consideration is the selection of the heat transfer fluid. Plants this size and smaller will use heat transfer fluids such as Dowtherm. However, large plants would benefit by using steam because of its better heat transfer properties.

Design Basis for a Large Metropolitan Area of 1,000,000

The major design feature of a large liquefaction system would be the use of a high temperature, high pressure stoker-fed steam boiler. This boiler could co-fire coal and could be equipped with scrubbers and other pollution control equipment. The basis design of the reactor itself can also be changed. In the smaller systems using electric, gas or heat transfer fluid for primary heating, the sludge was inside the pressure vessel and the heat has to be transferred through the thick-walled vessel. With a high pressure steam line, the steam and the sludge will both be inside the pressure vessel. This means that the pipe through which the sludge flows can be thinner and made from a high cost alloy such as Inconel. The sludge would be agitated inside the alloy pipe, the steam would be outside the alloy pipe and the steam and sludge would be enclosed by a large insulated carbon steel pressure vessel. The carbon steel vessel would be very thick in order to withstand the pressure. However, carbon steel is inexpensive and can readily be used in steam service whereas it cannot be used directly with sludge. The condensing steam on the alloy surface combined with a relatively thin alloy wall and scraped surface agitation of the sludge inside the pipe will result in high heat transfer rates. This heat transfer scheme will have heat transfer rates at least an order of magnitude greater than smaller systems using Dowtherm vapor and transferring heat through the pressure vessel. What this means is that the sludge can be heated in a highly efficient heat transfer device and then allowed to react in holding vessels. The bulk of the residence volume would be provided by these holding vessels. The holding vessels could be made of 24 inch nominal schedule 160 chrome-moly pipe or carbon steel pipe lined with stainless steel. The holding vessels would be maintained at temperature by steam trace heating on the exterior of the pipe. The holding vessels would not have scrapers.

Materials and Component Cost for a Large Metropolitan Area

The heating system for this large plant would be different from the previous smaller plants. The preheater would be similar in design but the high temperature heater would not be sized for the entire residence time. The high temperature heater would contain about one tenth the total residence volume. This large plant would be constructed from 24 inch or larger schedule 160 pipe. The heater, preheater and primary cooler would each be about 5 m long. About 40 m of pipe would be required for the high temperature residence zone. The entire reactor would require 7 segments; three 5 m long scraper surface heat transfer vessels and 4 eight ml holding vessels. This combines to a total of 47 m of pipe and weight of about 38 tonnes. The cost of the pipe alone, assuming the use of carbon steel costing $1.0 kg, would be about $38,000. This does not include the cost of lining the pipe with stainless steel or the cost of the fittings. However, the use of carbon steel pipe with a stainless steel liner made possible by the improved heat transfer consideration, will result in lower purchase and fabrication costs. Unlike chrome-moly steel, carbon steel pressure vessels do not require annealing after being welded. This is an important consideration given the size and weight of a 24 inch schedule 160 pipe. In addition, the improved heat transfer system eliminates the need for multiple scraper systems. Scrapers would be needed on the preheater and heater only and not on the residence vessels.

COST ESTIMATE SUMMARY

Table 32 provides a simplified check list of items included in the estimate of the fixed capital cost of the liquefaction process system for each size facility. The first part of the material cost list in Table 32 describes the costs incurred to obtain a building on-site to house the reactor system. The rest of table outlines the costs of each of the major components of the liquefaction system. The costs for the tanks were taken from reference 7. A present dollar conversion factor of 2.76 was used to update the costs. The cost of the reactor, a jacketed, high pressure, stirred kettle, was also taken from reference 7. Other values are based on our experience in purchasing components for the process development unit at Battelle-Northwest. The estimates presented in this chapter are preliminary budget estimates.

Table 33 shows a thermal analysis of the overall process and estimates the amount and value of excess oil for each size facility. The data used to determine the weights of char and oil produced by the process are as follows: The produced char and oil amounted to 15% and 25% of the weight of the dry feed sludge. The average heating values of the char and oil are 1.770 and 8,590 cal/g respectively. These figures combine to give the annual energy production. The energy required by the process was determined by assuming a net 150°C heat input to the process and an overall furnace and heating system efficiency of 65%. It was also assumed that all of the char would be burned first and then the oil would be consumed. We have assumed that the energy from the oil would be sold at a value of $\$4/10^6$ Btu. It is noteworthy that the energy recovered from this process is more than three times the theoretical amount needed to heat the sludge a net of 150°C. This provides considerable flexibility to the design of the furnace in that a high efficiency unit may not be required.

The summary table of capital and operating costs is shown in Table 34. This summary cost estimate is based on our best judgment at this time. The final result is a process that completely disposes of sludge for ca. $45/dry tonne for a large city. This amounts to roughly $11/tonne of 25% solids sludge and is almost competitive with ocean dumping and is less costly than incineration. Smaller plants are less economically feasible. (A more detailed comparison of liquefaction with other disposal methods will be highly site-specific and would be made on a case-by-case basis.)

TABLE 32. PURCHASED MATERIAL COST ESTIMATE

	Town - 10,000 Persons		City - 100,000 Persons		Metropolis - 1,000,000 Persons	
Item	Size Or Capacity	Cost Estimate	Size Or Capacity	Cost Estimate	Size Or Capacity	Cost Estimate
Land	Existing	--	.2 Ha	12,500	.5 Ha	100,000
Surveys	--	1,000	--	2,000	--	4,000
Fee and Permits	--	2,000	--	5,000	--	10,000
Site Preparation		4,000		6,000		20,000
Foundation	10mX15m 10 tonnes	15,000	10mX15m 40 tonnes	15,000	30mX30m 100 tonnes	75,000
Process Building	10mX10mX10m steel sheet sides	50,000	10mX15mX20m steel sheet sides	100,000	20mX15mX20m steel sheet sides	200,000
Crane	5 tonnes	12,000	10 tonnes	20,000	25 tonnes	40,000
Plumbing	water, nitrogen compressed air	8,000	water, nitrogen compressed air	10,000	water, nitrogen compressed air	17,500
Ventilation	1000 cubic meters per hour	3,000	3000 cubic meters per hour	6,000	10,000 cubic meters per hour	15,000
Fire Protection System	per code	4,000	per code	8,000	per code	20,000
Lighting	indoor/outdoor sodium vapor	4,000	indoor/outdoor sodium vapor	4,000	indoor/outdoor sodium vapor	8,000
Communications	public address and warning	1,000	public address and warning	1,000	public address and warning	2,000
Sludge Preparation Subsystem	15 liters/min	7,500	150 liters/min	20,000	1500 liters/min	75,000
Sludge Injection Subsystem	2000 psig 3 liters/min	10,000	2000 psig 30 liters/min	30,000	2000 psig 300 liters/min	150,000
Reactor & Cooler Subsystem	275-310°C 3 liters/min	200,000	275-310°C 30 liters/min	400,000	275-310°C 300 liters/min	2,200,000
Let Down Subsystem	3 liters/min	20,000	30 liters/min	50,000	300 liters/min	200,000
Product Recovery Subsystem	5000 liters 3 liters/min	15,000	50,000 liters 30 liters/min	60,000	100 meters 300 liters/min	200,000
Primary Heating System	40 Mcal/hour	30,000	400 Mcal/hour	4,120,000	4.0 Gcal/hour	800,000
Ash Handling	200 kg/hr	1,000	2 tonnes/hr	7,000	10 tonne/hr	30,000
Process Integration Piping	as needed	12,500	as needed	35,000	as needed	100,000
Instrumentation and Control	computerized with manual override	60,000	computerized with manual override	90,000	computerized with manual override	150,000
Electric Utility Hookup	480 volt	10,000	480 volt	30,000	480 volt	50,000
Material Subtotal		470,000		1,031,500		4,466,500

TABLE 33. ENERGY REQUIREMENTS AND OUTPUTS OF THE SLUDGE TO OIL FACILITIES

	Town - 10,000		City - 100,000		Metropolis - 1,000,000	
Operating Element	Heat Value	Annual Energy Kcal	Heat Value	Annual Energy Kcal	Heat Value	Annual Energy Kcal
Energy Input of Sludge	3300	9.64E+08	3300	9.64E+09	3300	964E+10
Heat Used In Process		3.54E+08		3.54E+09		3.54E+10
Energy In Char	1770	7.76E+07	1770	7.76E+08	1770	7.76E+09
Energy In Oil	8590	6.27E+08	8590	6.27E+09	8590	6.27E+10
Energy of Excess Oil		6.27E+08		3.51E+09		3.51E+10
Amount of Excess Oil		83 tonnes/yr		416 tonnes/yr		4160 tonnes/yr
Value Of Excess Oil			$4.00/MMBtu	$55,672	$4.00/MMBtu	$556,719

TABLE 34. COST ESTIMATE COMPARISON FOR THREE DIFFERENT SIZES OF FACILITIES

	Town - 10,000		City - 100,000		Metropolis - 1,000,000	
Capital Cost Element STORS	Percent of Capital Cost	Estimated Cost	Percent of Capital Cost	Estimated Cost	Percent of Capital Cost	Estimated Cost
Engineering Design	15	$100,000	13	$ 200,000	8	$ 500,000
Purchased Materials	68	$470,000	66	$1,031,500	69	$4,466,500
Construction Labor	11	$ 75,000	16	$ 250,000	15	$1,000,000
Construction Management	4	$ 25,000	3	$ 40,000	2	$ 150,000
Start-Up Materials	1.02	$ 7,000	0.64	$ 10,000	3	$ 200,000
Indirect Capital Costs	1.46	$ 10,000	1.48	$ 23,000	3	$ 170,000
Capital Cost	100	$687,000	100	$1,554,500	100	$6,116,500

Operating Cost Element STORS	Percent of Operating Cost	Estimated Annual Cost	Percent of Operating Cost	Estimated Annual Cost	Percent of Operating Cost	Estimated Annual Cost
Debt Service at 8%, 20 years	39.9	$ 69,972	41	$158,329	35	$ 660,664
Maintenance Labor and Supplies	14.2	$ 25,000	6	$ 25,000	5	$ 100,000
Operator Labor	22.8	$ 40,000	21	$ 80,000	13	$ 250,000
Fuel and Soda Ash	8.5	$ 15,000	26	$100,000	40	$ 750,000
Miscellaneous Supplies	14.2	$ 25,000	6	$ 25,000	5	$ 100,000
Indirect Maintenance	0.1	$ 200	0	$ 600	0	$ 3,600
Indirect Operating Cost	0.2	$ 300	0	$ 1,000	0	$ 2,800
Annual Operating Cost	100	$175,472	100	$389,929	100	$1,867,064
Annual Operating Revenue		$ 0		$ 55,672		$ 556,719
Net Annual Cost		$175,472		$334,257		$1,310,345
Sludge Disposal Cost $/T (Dry)		$ 601		$ 114		$ 45

INCREMENTAL ANNUAL TREATMENT PLANT COSTS	Estimated Annual Cost	Estimated Annual Cost	Estimated Annual Cost
Operating and Maintenance	$56,000	$130,000	$ 600,000
Amortized Capital	$37,000	$ 85,000	$ 400,000
Total Incremental Cost	$93,000	$215,000	$1,000,000
Incremental Sludge Disposal Cost $/T (Dry)	$ 318	74	34

The indirect costs of the waste liquor recycle were derived from reference 8 with some adjustment of the basis of calculation. Reference 8 shows a graph of incremental indirect O&M costs versus on gallons of recycle liquor and on million gallons per day of capacity. The basis sludge in reference 8 contained 4.5% solids whereas the basis sludge for the STORS process contains 20% solids. The cost figures were determined by estimating the gallons per minute of recycle liquor from the STORS process and adjusting the flow rate for an estimated 9% downtime. The capital costs were estimated by back calculating the total sewage flow into the treatment plant based on the given figure of 1.1 tons of solids per million gallons per day of wastewater. This total sewage flow figure was then reduced by a factor of 4.5%/20% to account for the difference in the water content in the sludge.

SECTION 7

OVERALL ACHIEVEMENT OF PROJECT OBJECTIVES

This project was designed to evaluate a promising batch process for sludge disposal on a continuous scale. Although some specific goals have not been met, the overall result of the research was highly favorable: Liquefaction of a municipal primary sludge was achieved on a continuous basis for over 100 hours total in a prototype reactor, without major problems in clogging, char deposition, or corrosion. Process parameters were defined, and product behavior and properties characterized. An overall yield of 73% of the dry feed sludge energy content in the form of separable oil and char appears to be readily achievable on a larger scale, with product oil having a heating value of about 8800 cal/g. Wastewater was found to be readily treatable by current practice, although heavily loaded with organic materials, and the off-gas represents no environmental threat, being mostly carbon dioxide and of low volume. A preliminary economic estimate based on realistic assumptions and the experimental data reported here gives a sludge disposal cost of $45/dry tonne for a city of one million people, with a capital cost of $6.1M. If municipal garbage can also be fed to the system, economics become even more favorable, and will permit application of the process to even smaller communities.

To continue this work to the point where a pilot plant could be built, additional research is needed. Some of the items which require further investigation are as follows:

* Optimum liquefaction parameters: Our initial estimates were too pessimistic; complete conversion of sludge occurred under temperature, pressure, and residence time conditions which were much milder than anticipated. In particular, the effects of reduced residence times and alkali concentration need further investigation.

* Material balances, both organic and inorganic. Mixing occurred to a greater extent than anticipated, a problem which should not occur in the modified reactor. There were indications that the liquefaction process may be useful in destroying organic toxic materials and concentrating inorganic heavy metals in the ash and char fraction and away from the wastewater.

* Product separation and stability. Initial product separation from wastewater was not good, but this was corrected by modifying reactor conditions, and good separation occurred rapidly and spontaneously in later runs. The separation process requires further study to determine exact conditions,

possibly leading to patentable information. Properties of separated oil, as opposed to solvent-extracted oil, need to be examined. Limited results obtained to date on separated oil indicate that it is much less viscous than extracted oil. The variation of oil viscosity with storage time and the effect of vacuum distillation to make a light (#2) product also need further work.

* Addition of a comminution device should allow work on liquefaction of other materials such as garbage. This would greatly extend the range of application for the process.

* Longer duration runs need to be performed to obtain data on corrosion, erosion, mineral settling, and char buildup. Although no problems were encountered in 100 hr of operation of the reactor, this is insufficient to identify long-term materials behavior problems.

Previous work by others (1) used a dried sludge which was liquefied in an organic solvent with a nickel catalyst, or is an aqueous sludge slurry at 400°C, with hydrogen. The economic cost of either pre-drying or hydrogen addition is prohibitive. Solvent recovery is also costly. The STORS process uses only conventional dewatering of primary sludge to 20% solids, and a cheap catalyst (sodium carbonate), with no hydrogenation, at a much lower temperature (275°C). It is consequently much more competitive economically. If a higher quality oil is required, it is more cost-effective to upgrade the STORS product than to apply hydrogenation to the whole system, including water. Consequently we feel that the simpler the liquefaction process, the more chance it has of commercialization.

In a society where sludge disposal is an ever-growing problem, the liquefaction technique offers a flexible, safe, and economical alternative to incineration and should be pursued further.

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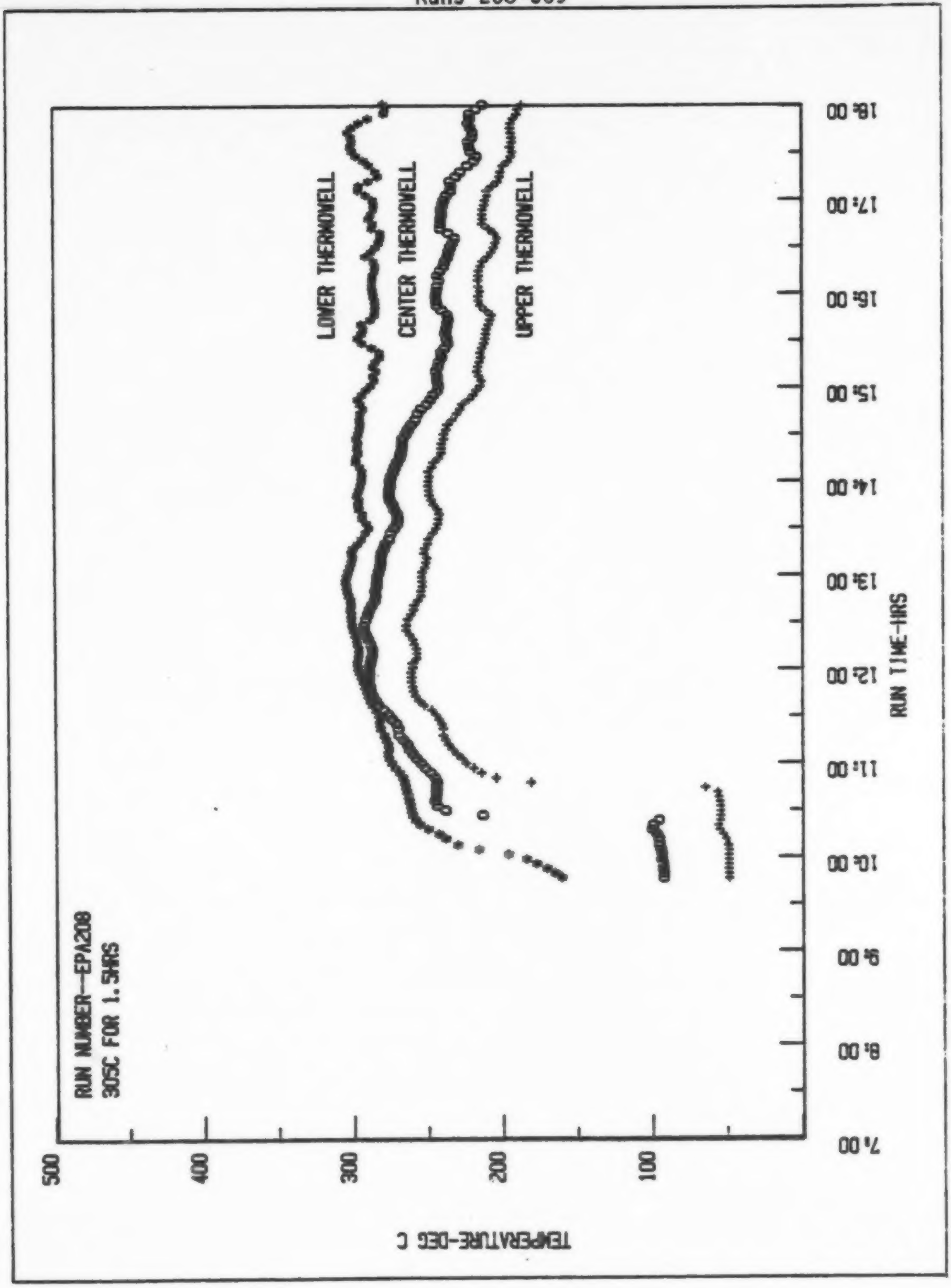
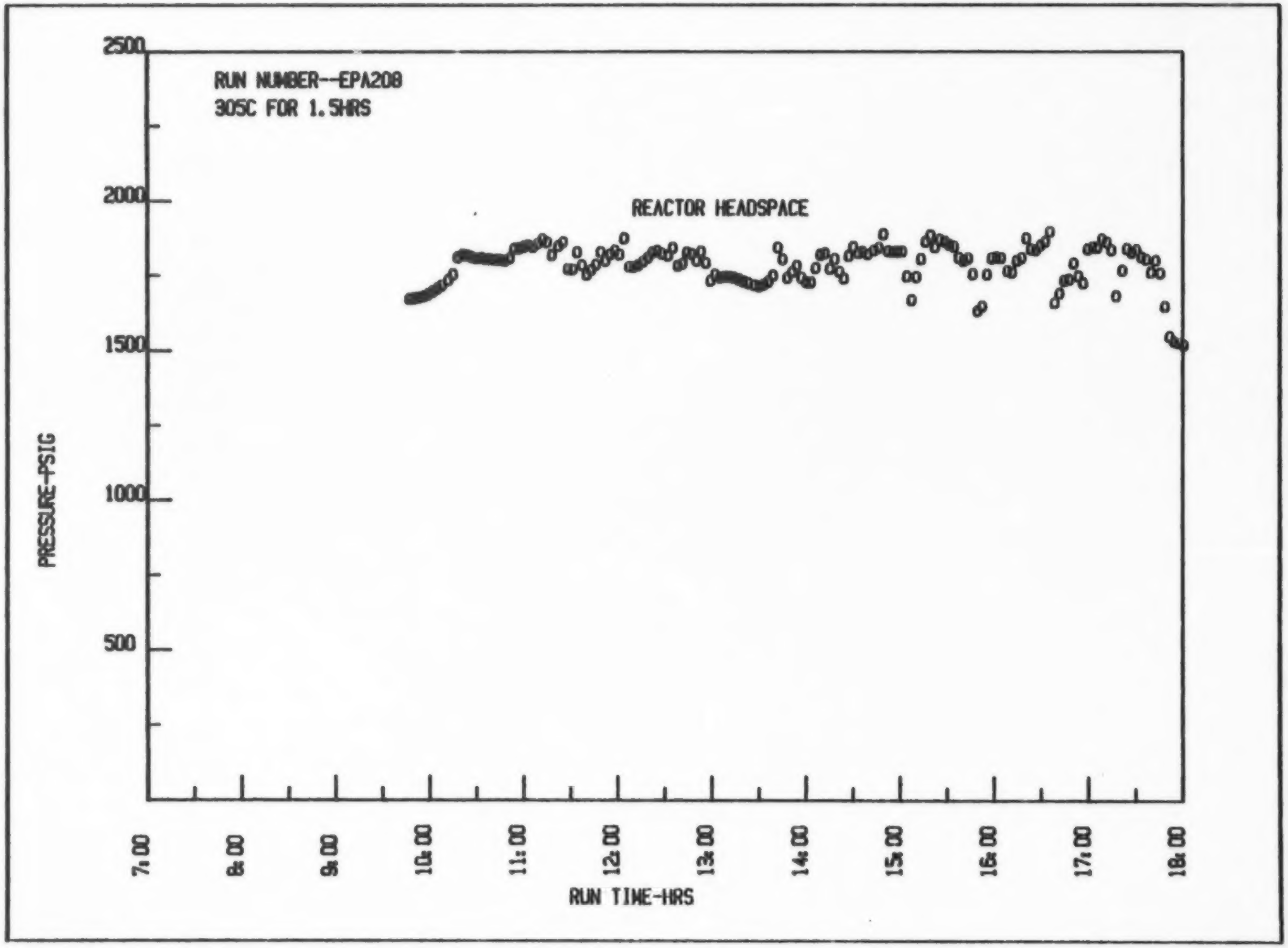
APPENDIX A

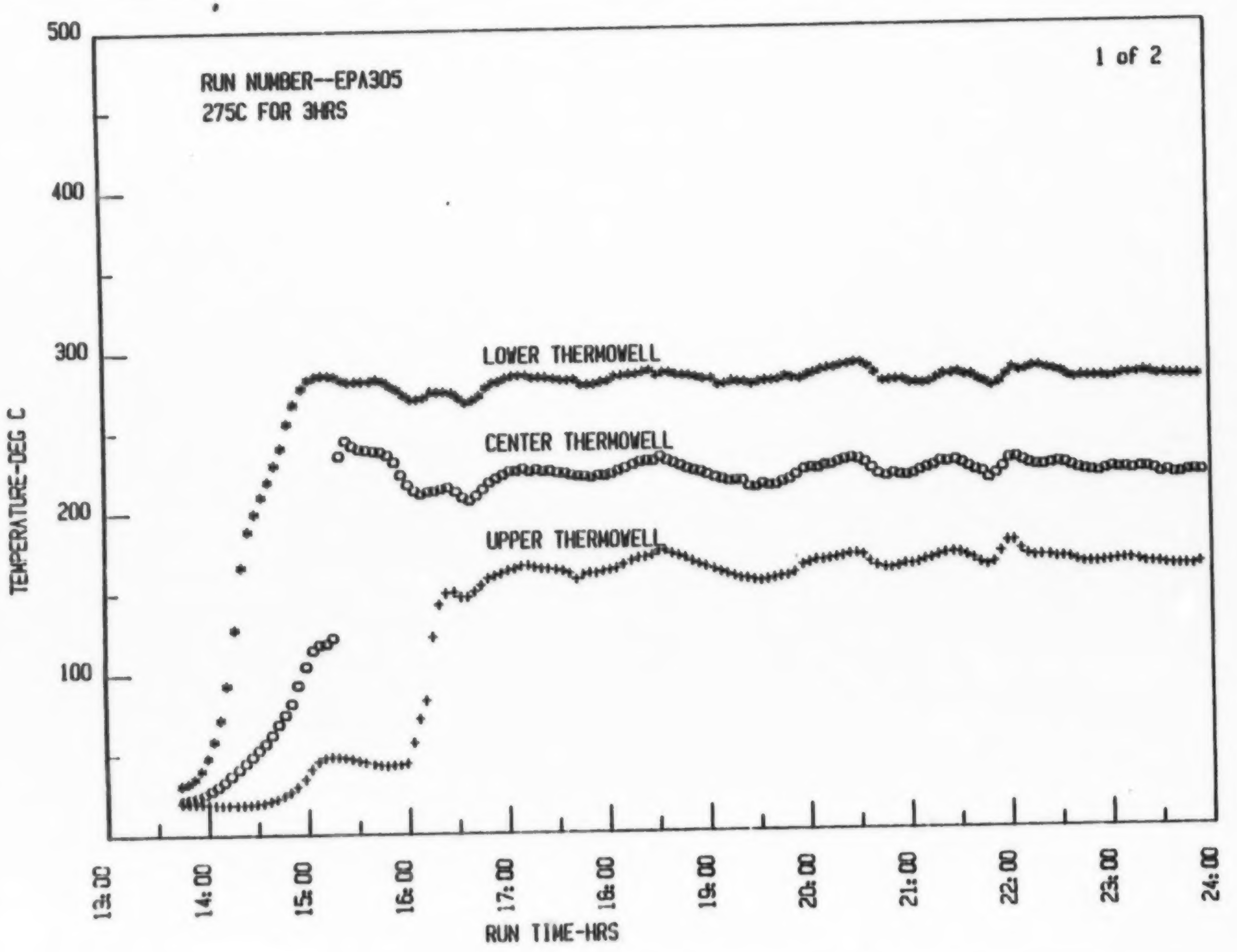
Reactor Temperature and Pressure Profiles
Runs 208-509



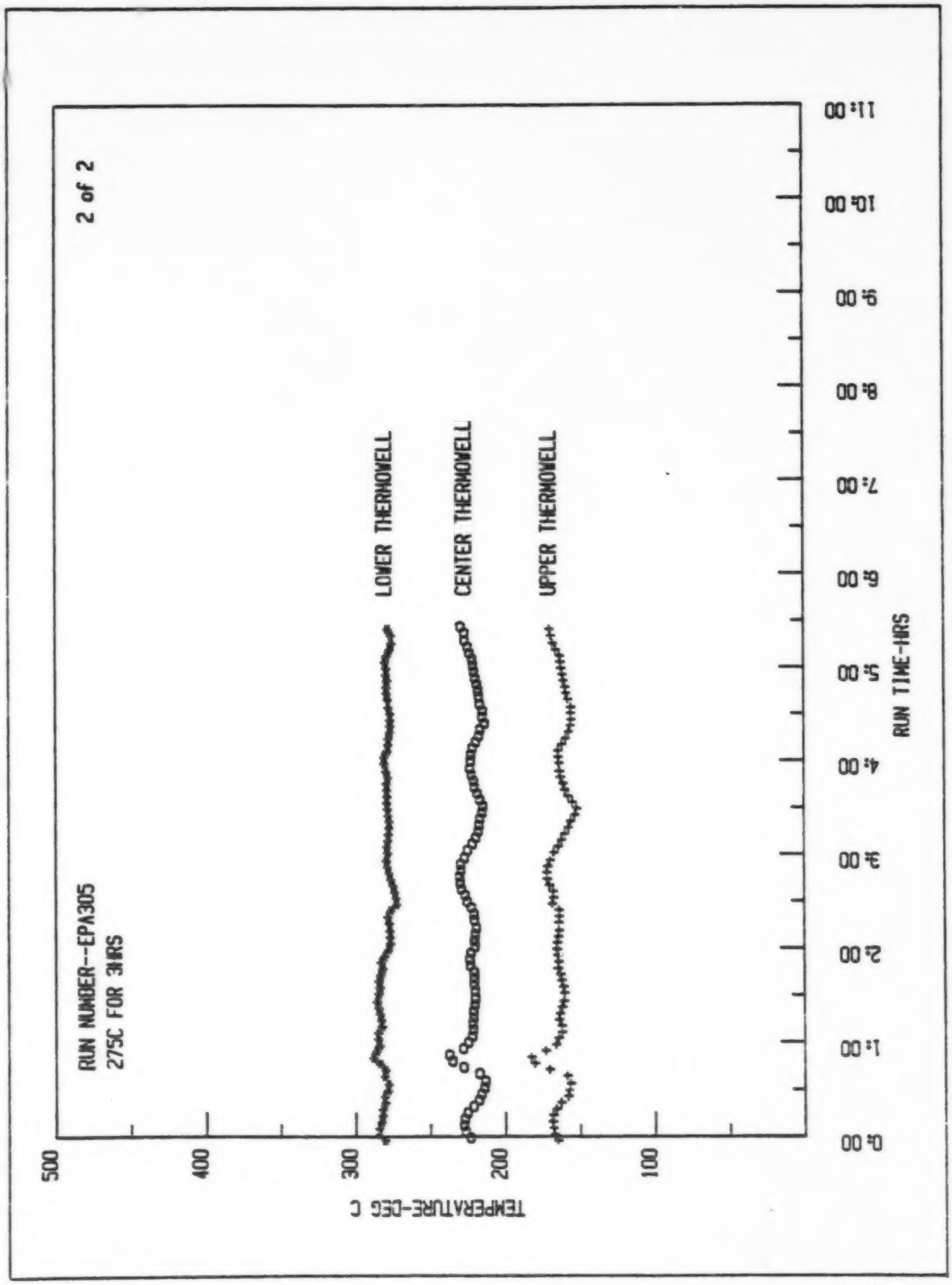
Reaction Temperature and Pressure Profile, Run 208

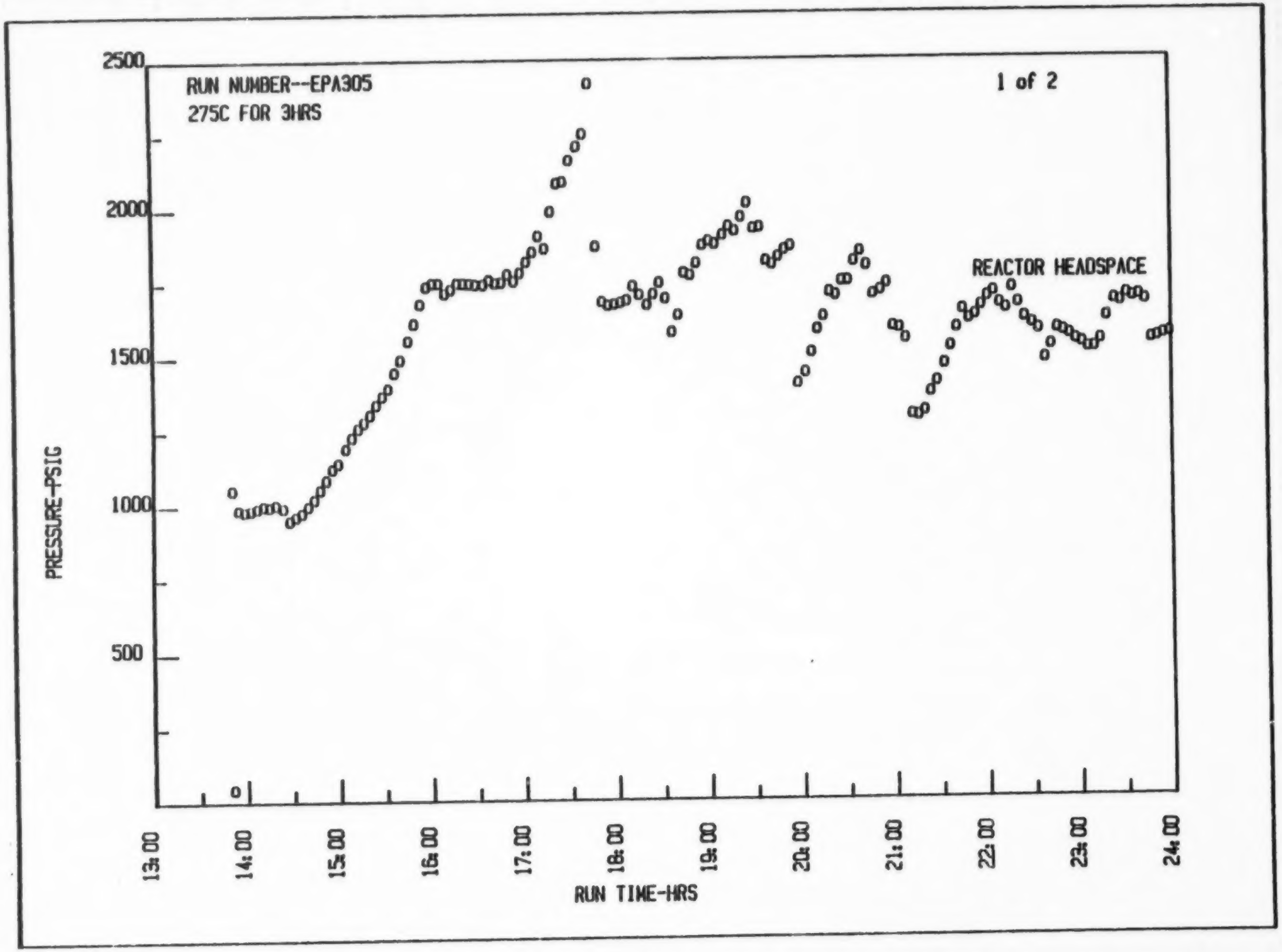


Reaction Temperature and Pressure Profile, Run 208

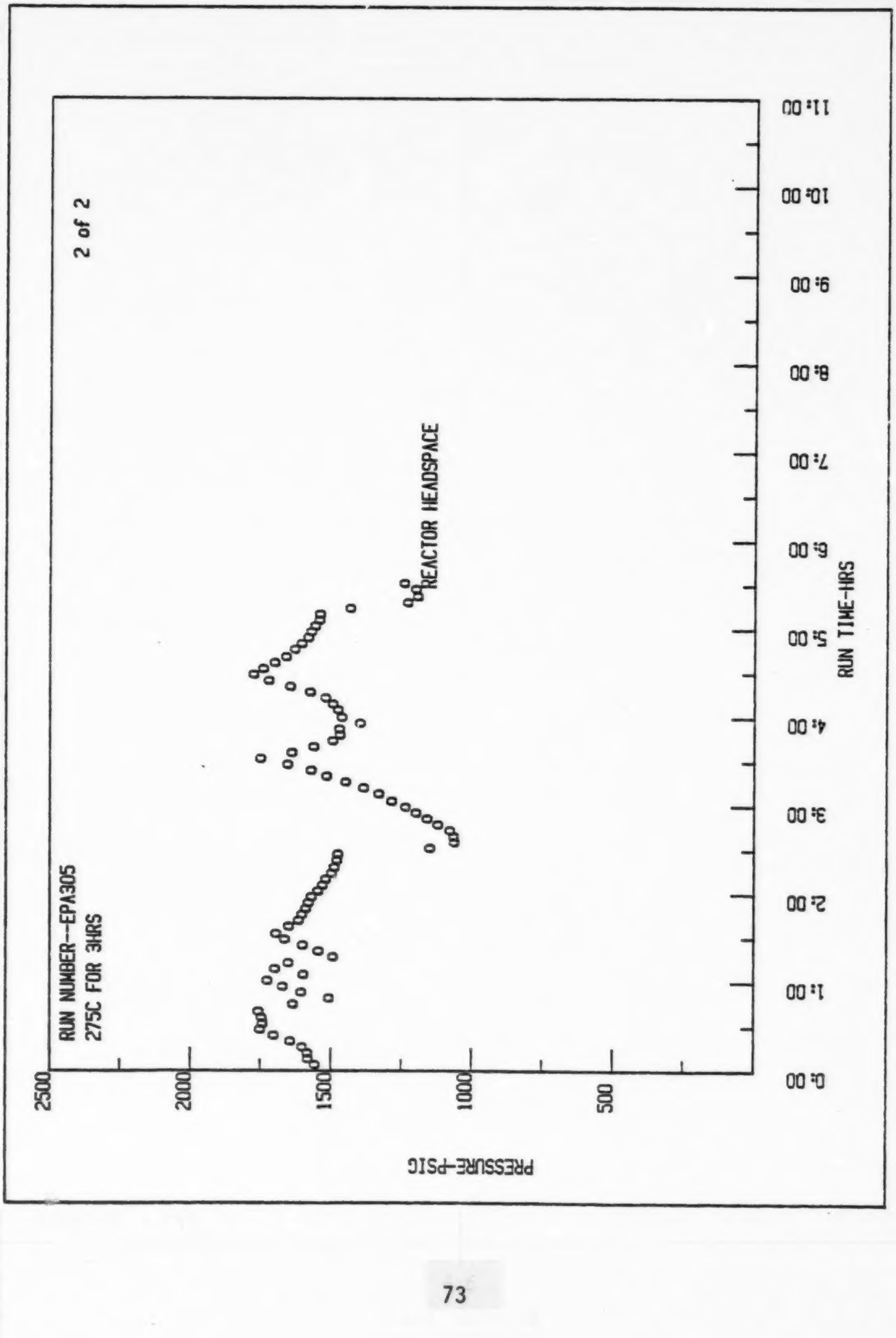


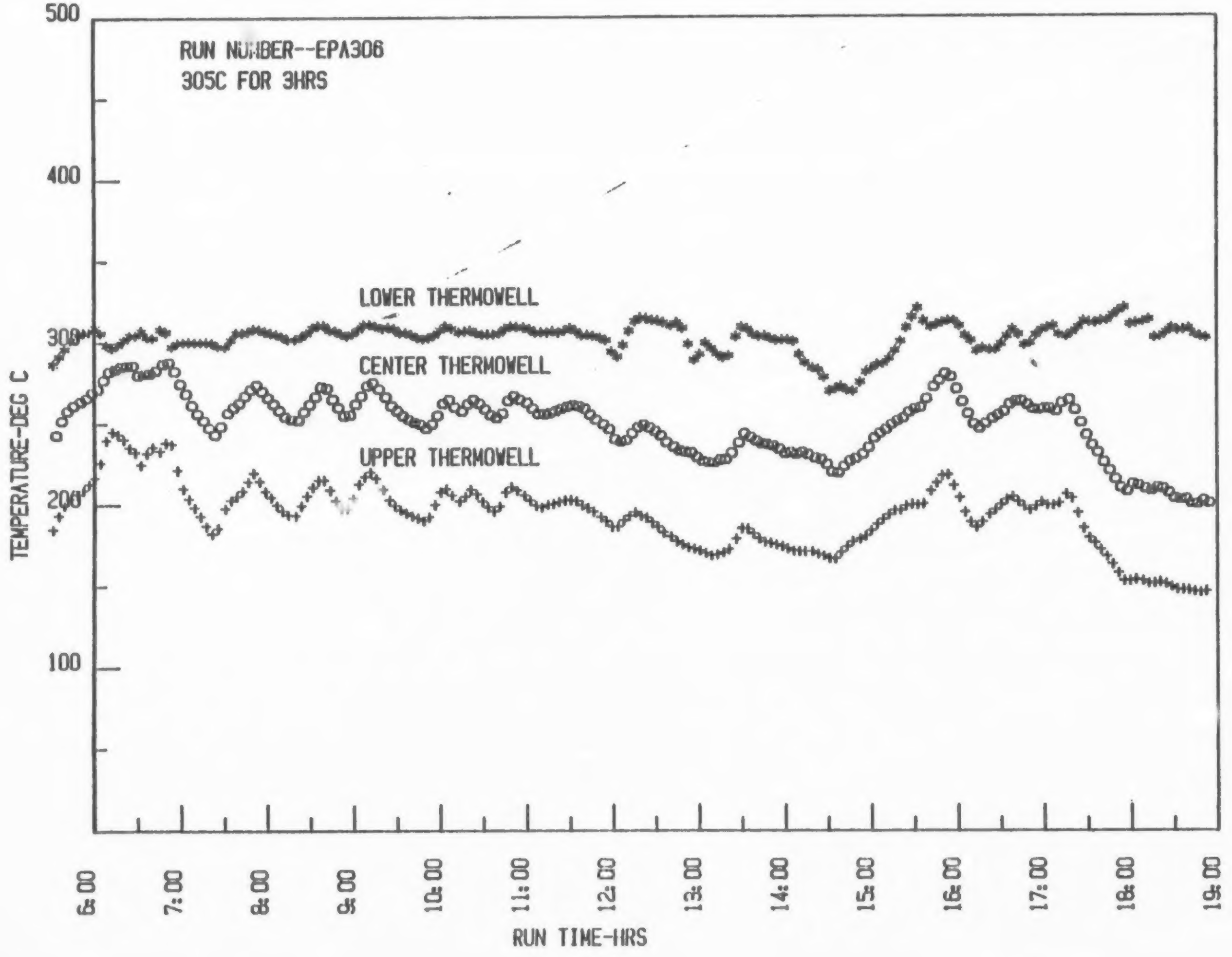
Reaction Temperature and Pressure Profile, Run 305


RUN NUMBER--EPA305
275C FOR 3HRS
2 of 2
LOWER THERMOWELL
CENTER THERMOWELL
UPPER THERMOWELL
TEMPERATURE-DEG C
500
400
300
200
100
RUN TIME-HRS
0:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00

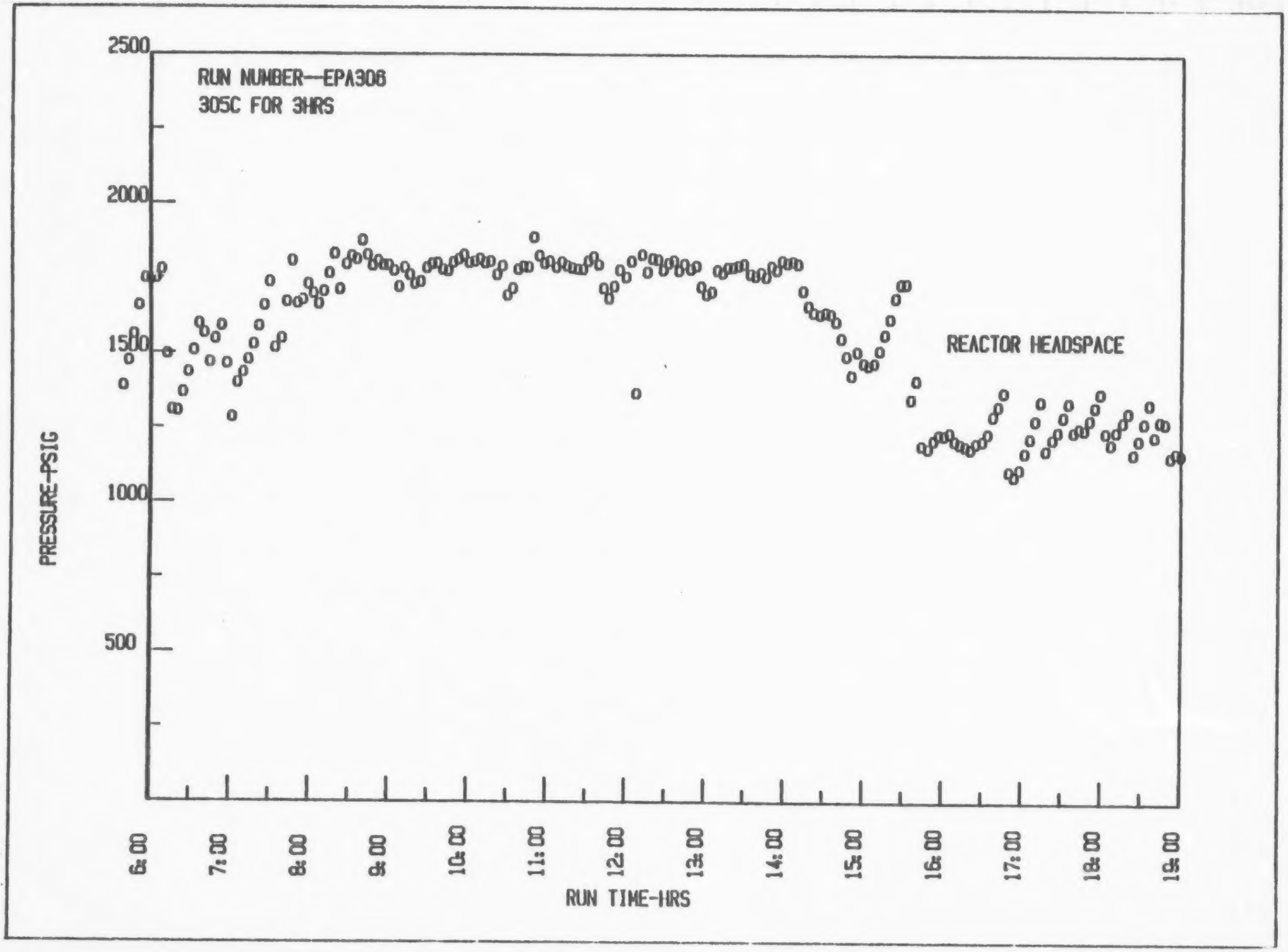


Reaction Temperature and Pressure Profile, Run 305

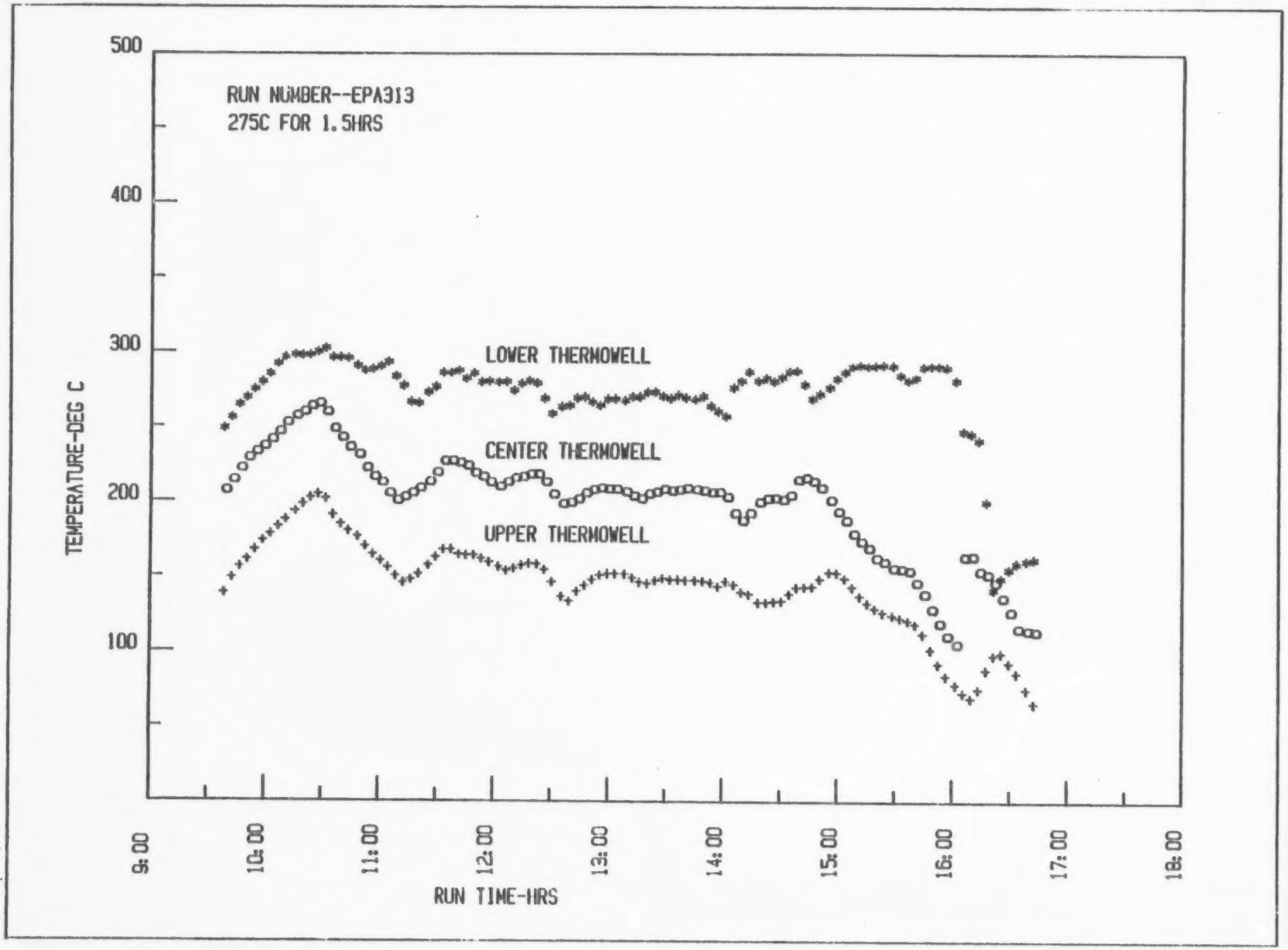

RUN NUMBER--EPA305
275C FOR 3HRS
2 of 2
REACTOR HEADSPACE
PRESSURE-PSIG
2500
2000
1500
1000
500
RUN TIME-HRS
0:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00



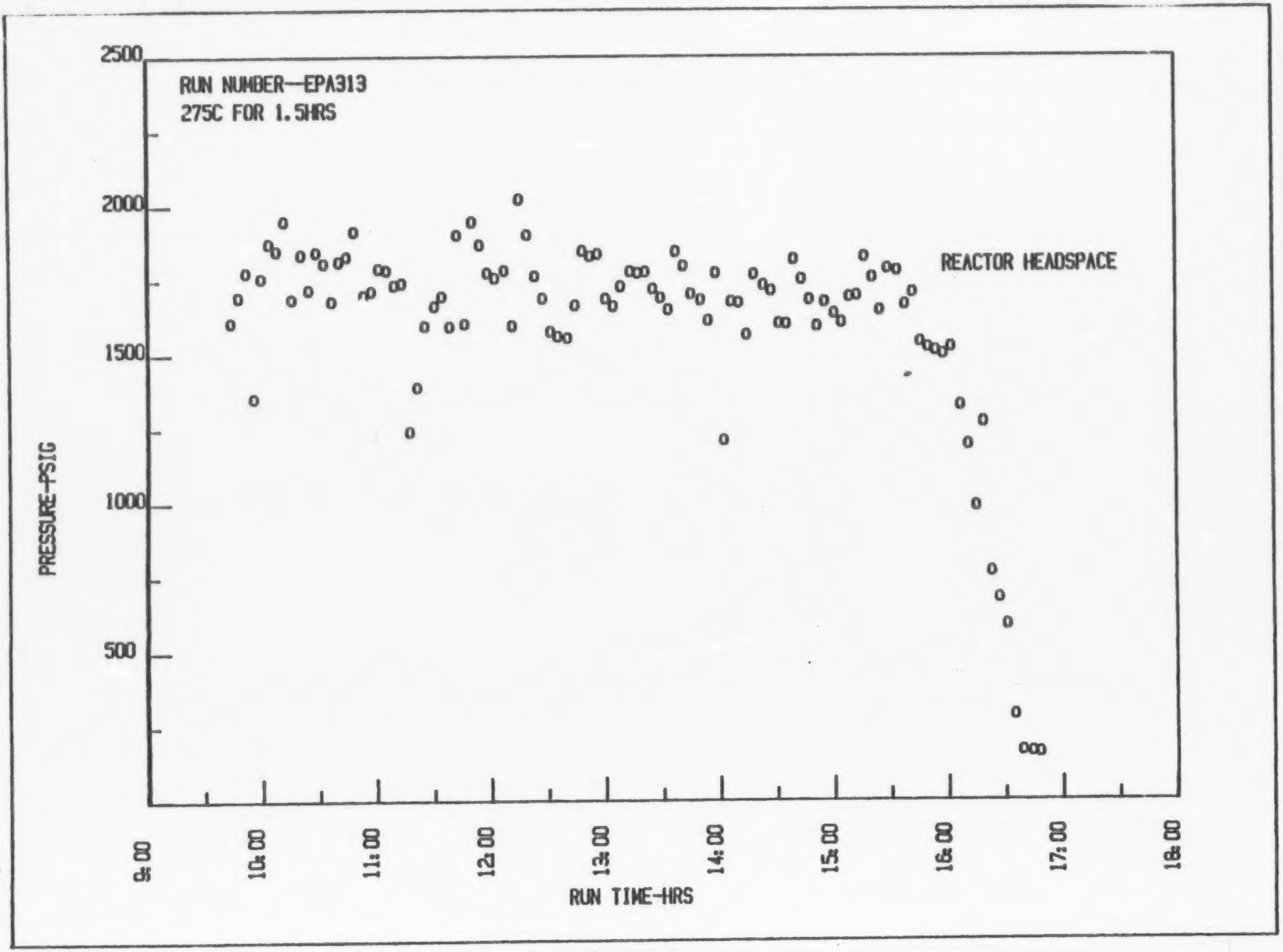
Reaction Temperature and Pressure Profile, Run 306



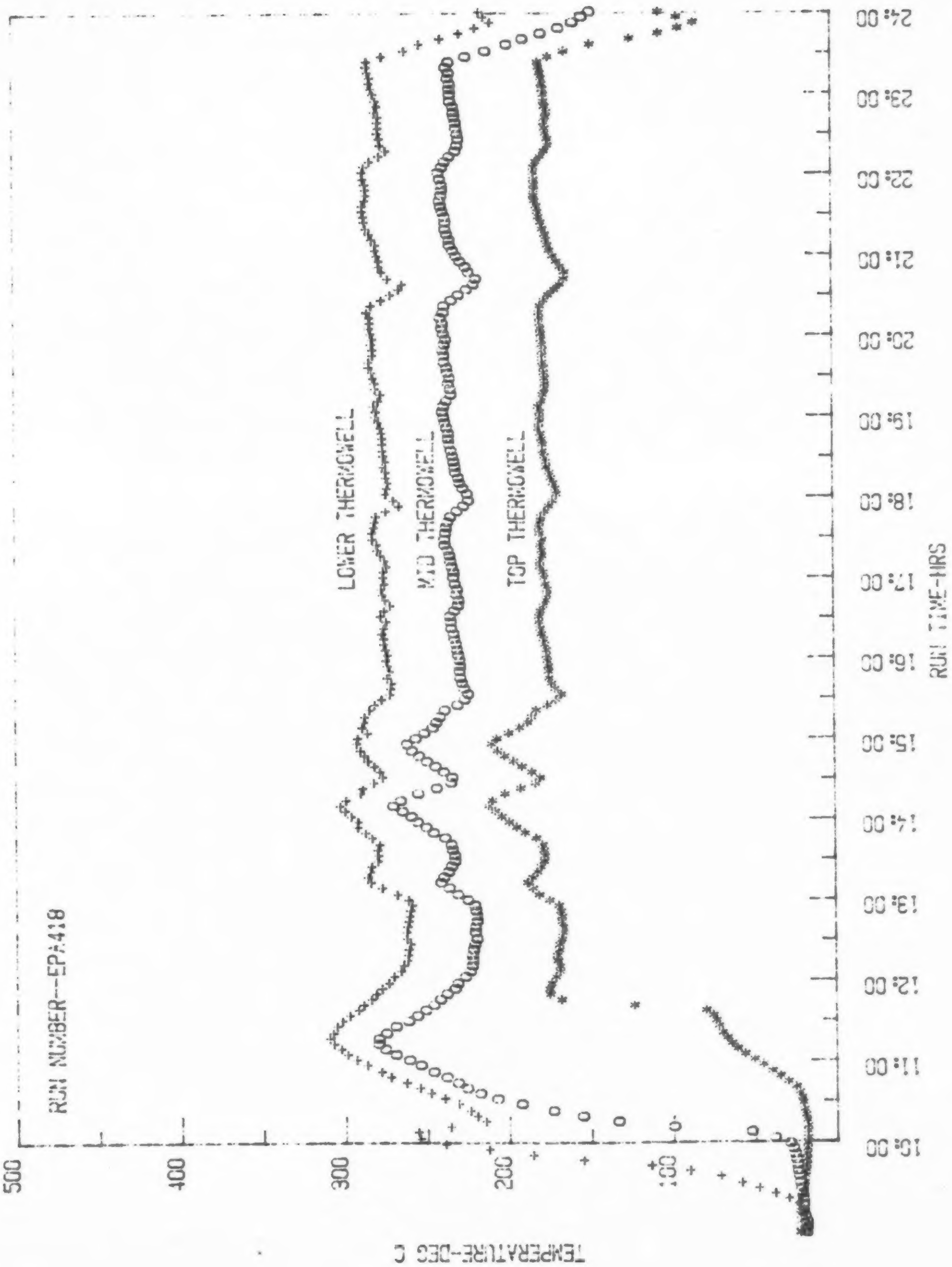
Reaction Temperature and Pressure Profile, Run 306



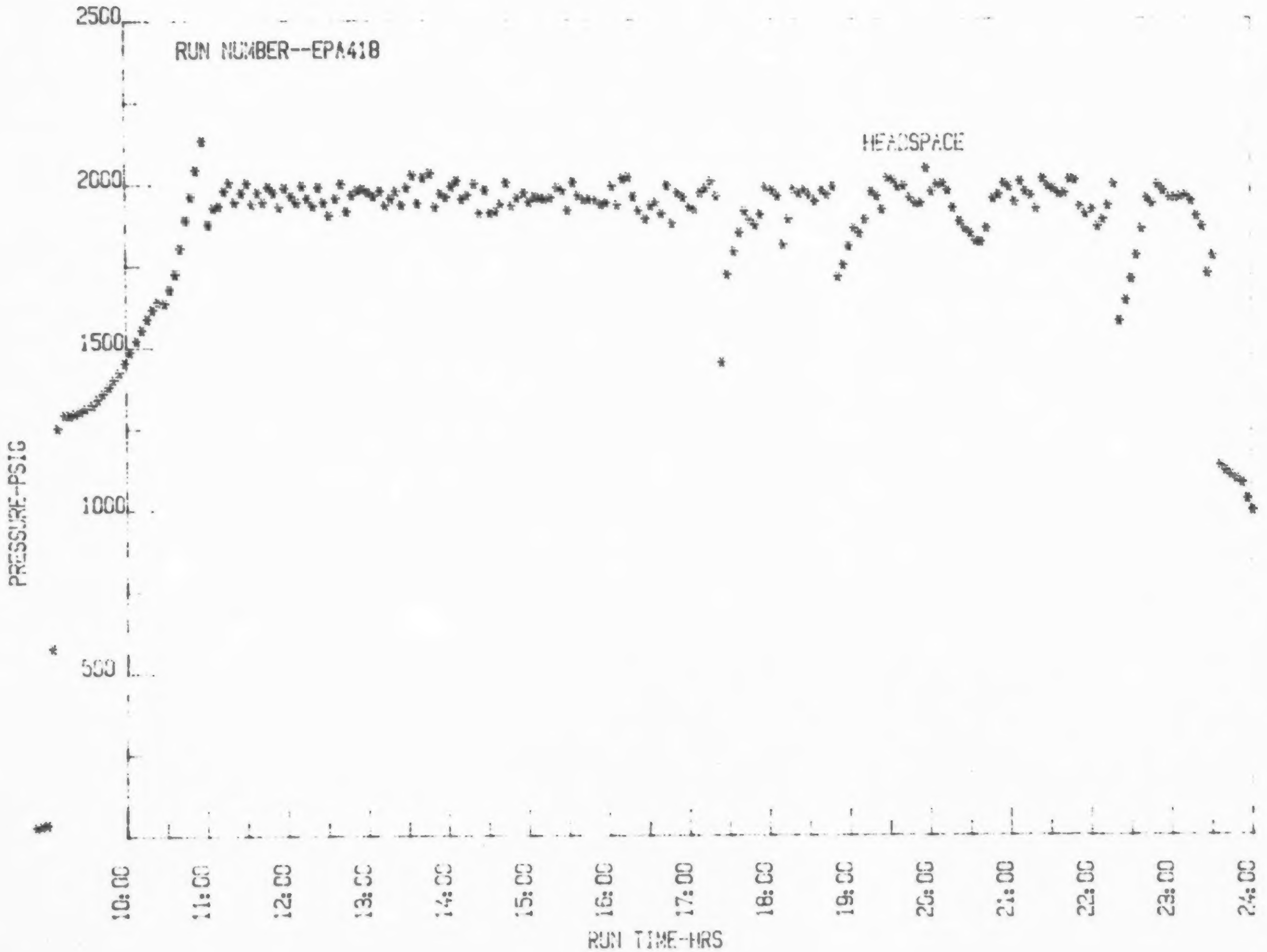
Reaction Temperature and Pressure Profile, Run 313



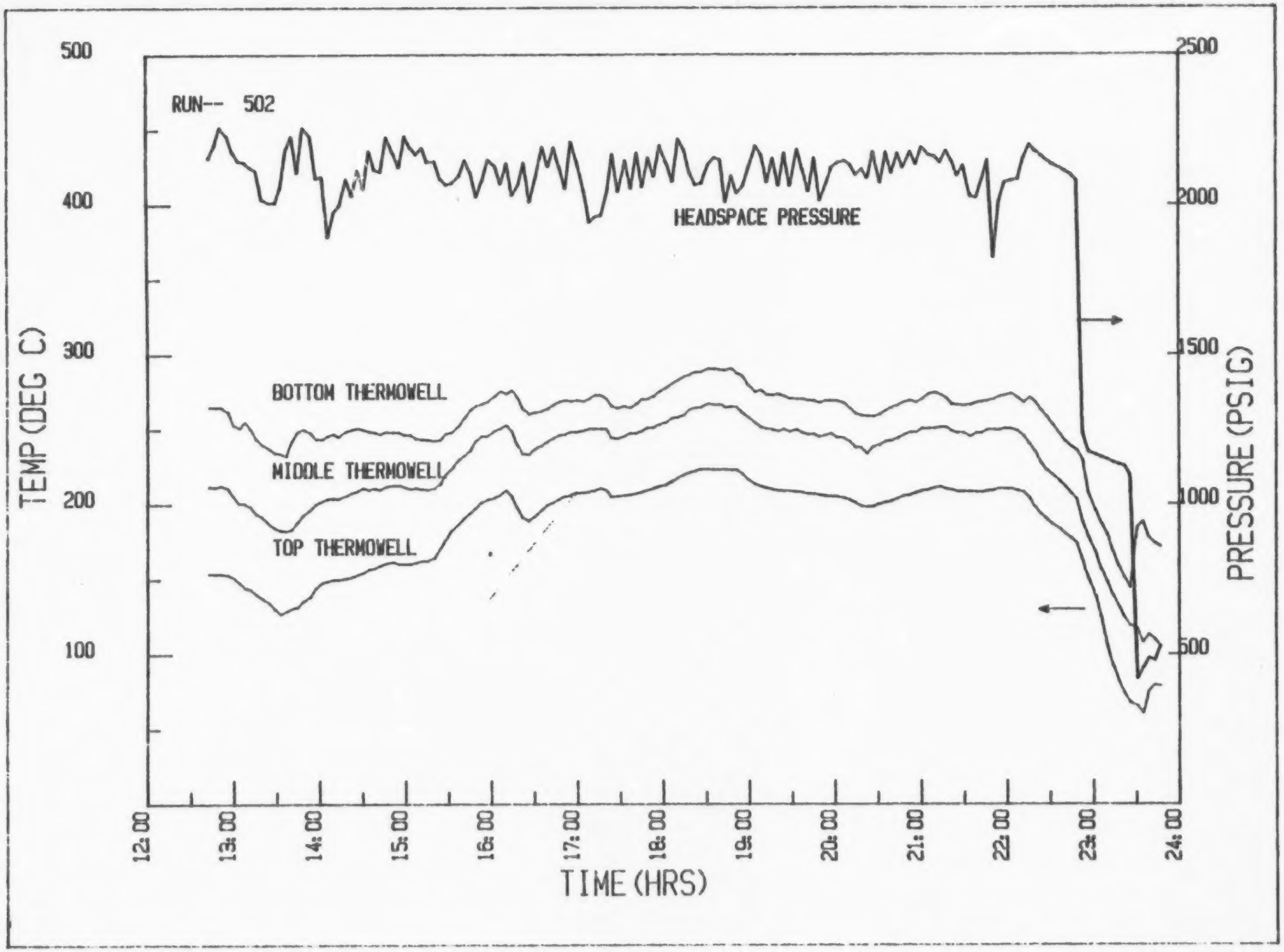
Reaction Temperature and Pressure Profile, Run 313



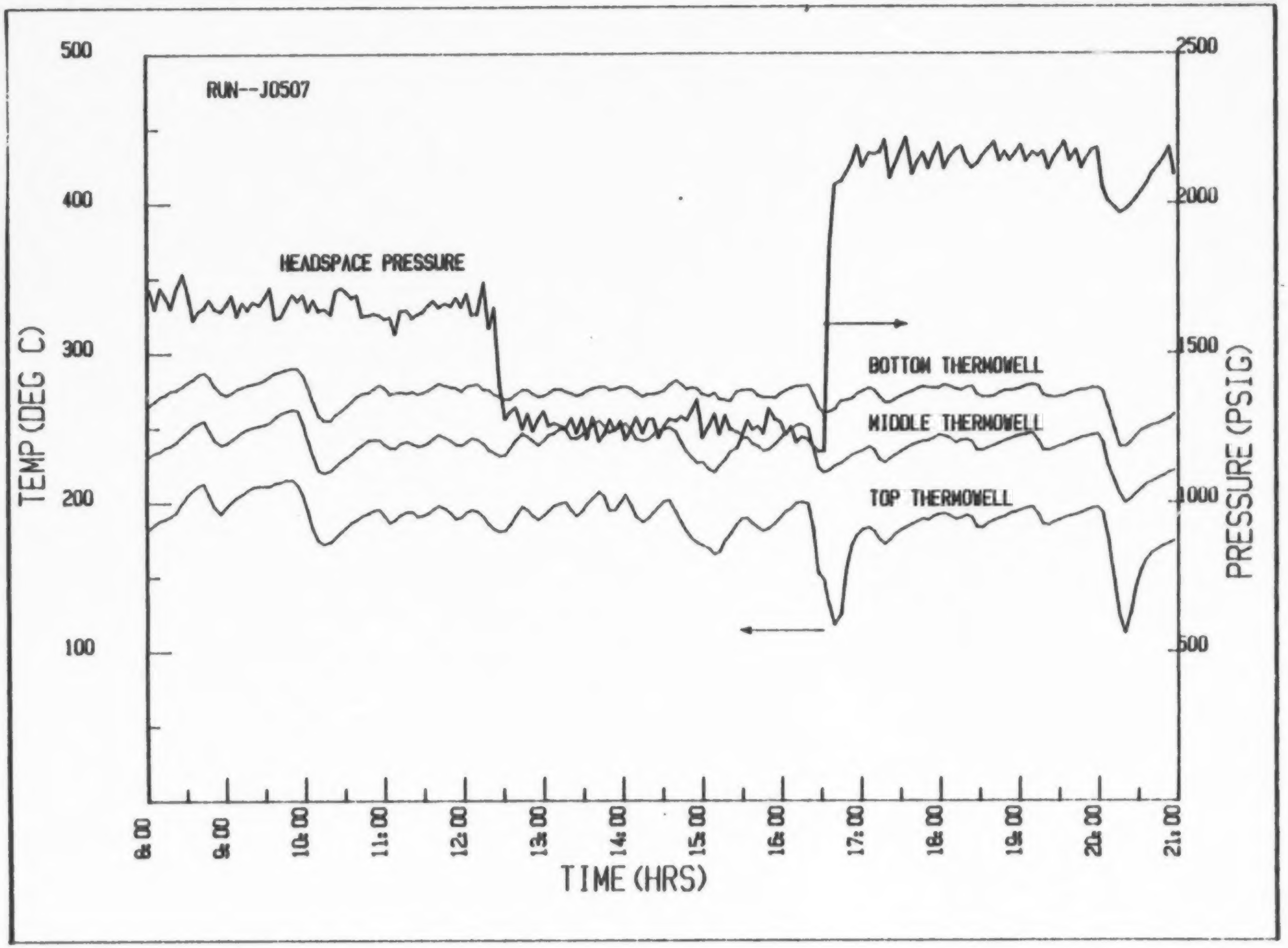
Reaction Temperature and Pressure Profile, Run 418



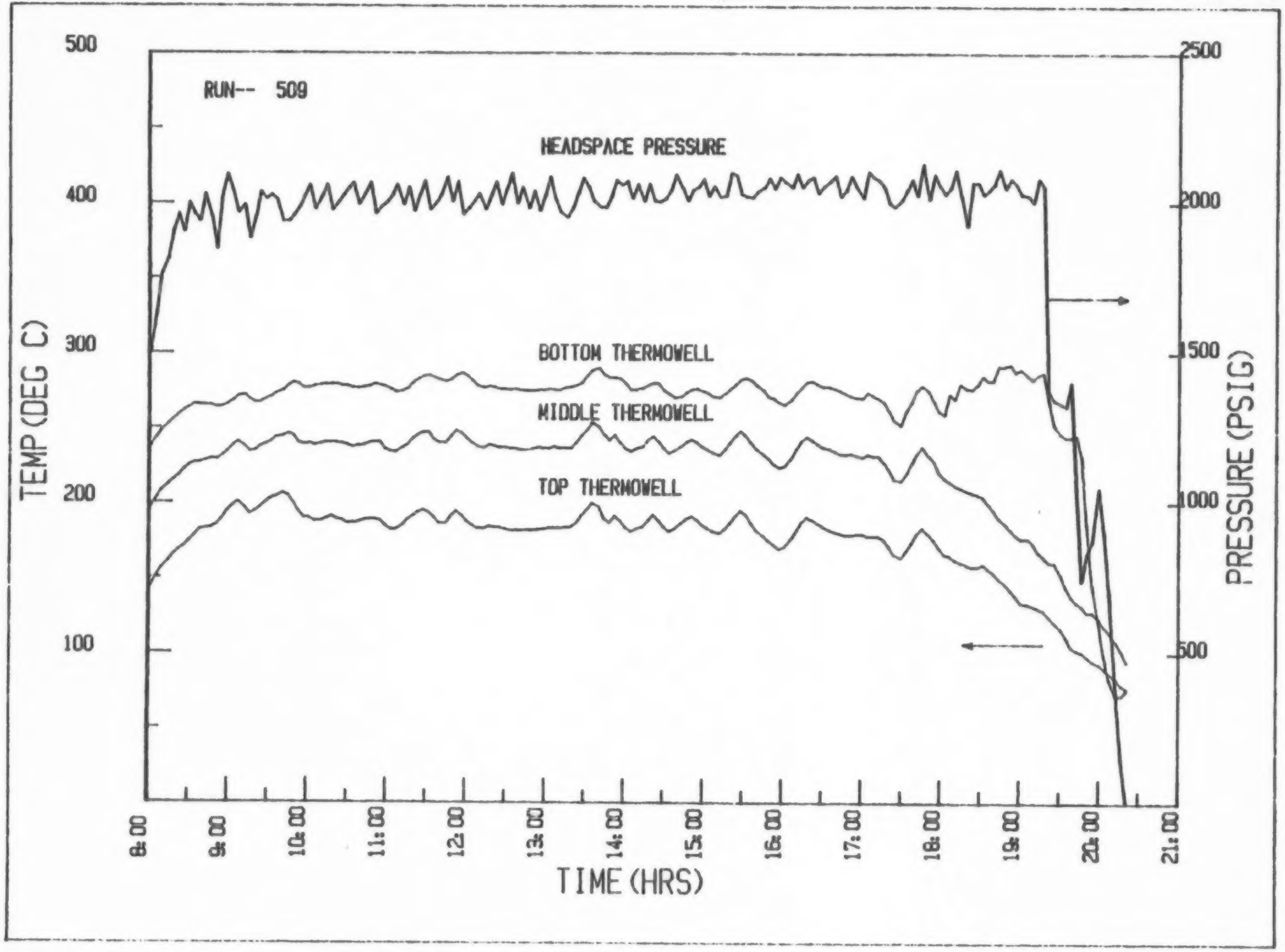
Reaction Temperature and Pressure Profile, Run 418



Reaction Temperature and Pressure Profile, Run 502



Reaction Temperature and Pressure Profile, Run 507



Reaction Temperature and Pressure Profile, Run 509

APPENDIX B

Detailed Inorganic Elemental Analyses

B-1. Trace Element Concentrations in Feedstock Sludges

SOURCE	RUN #	208		305		306		313		418 #1		418 #2		502		507		509	
	ELEMENT	CONCN. PPM.	±																
Zr	V	<23.		<17.		<17.		<16.		22.3	9.7	18.8	9.3	<17.		<16.		<17.	
	Cr	179.	12.	82.1	6.6	541.	29.	80.5	6.8	103.1	8.2	96.5	7.8	97.6	7.2	112.4	7.9	100.9	7.7
	Mn	136.8	9.0	80.9	6.0	95.6	7.1	64.6	5.3	2.3	6.3	72.0	5.8	69.8	5.5	74.4	5.5	81.3	6.0
	Ni	25.1	2.4	17.3	1.9	20.1	1.5	17.9	1.4	27.9	2.4	37.2	2.6	26.9	2.1	22.7	1.6	20.8	1.6
	Cu	690.	35.	480.	24.	309.	16.	286.	15.	339.	17.	399.	20.	302.	15.	290.	15.	296.	15.
	Zn	1122.	56.	575.	29.	616.	31.	516.	26.	651.	33.	686.	34.	662.	33.	653.	33.	772.	39.
	Ga	3.57	0.72	4.28	0.58	1.92	0.51	2.01	0.52	3.29	0.62	2.18	0.53	2.29	0.52	2.04	0.50	2.51	0.55
	Se	4.50	0.44	3.93	0.40	2.29	0.33	2.51	0.36	3.39	0.45	2.92	0.34	2.64	0.35	3.24	0.35	3.03	0.36
	Pb	146.3	7.5	75.3	4.0	58.8	3.2	59.1	3.3	53.7	3.1	54.4	3.0	52.4	2.9	55.3	3.0	59.0	3.2
	As	2.6	1.1	2.29	0.81	<1.3		1.59	0.75	2.63	0.86	2.79	0.69	1.75	0.69	1.40	0.69	1.77	0.74
	Br	12.73	0.79	7.58	0.55	5.67	0.47	6.62	0.51	8.33	0.62	9.04	0.59	6.93	0.51	6.35	0.49	6.76	0.51
Ag	Rh	4.52	0.79	7.59	0.90	3.67	0.73	<1.5		5.01	0.50	3.67	0.68	3.38	0.71	4.31	0.72	4.28	0.75
	U	7.1	1.3	7.4	1.4	10.3	1.4	8.4	1.4	6.8	1.4	7.0	1.2	7.5	1.3	6.6	1.2	8.1	1.3
	Sr	153.	11.	105.7	7.5	87.5	6.2	77.0	5.5	101.9	7.2	100.0	7.1	80.6	5.7	81.2	5.7	93.6	6.6
	Y	2.65	0.70	3.37	0.70	3.00	0.68	1.90	0.73	3.17	0.72	2.21	0.59	3.32	0.65	2.69	0.63	2.45	0.66
	Zr	542.	38.	498.	35.	802.	56.	939.	66.	747.	52.	635.	44.	529.	37.	493.	35.	514.	36.
	Nb	<1.1		<1.2		<1.2		<1.3		1.59	0.65	1.51	0.53	<1.1		<1.1		<1.2	
	Mo	12.4	1.3	11.6	1.3	14.7	1.6	15.6	1.7	12.3	1.5	19.1	1.7	12.0	1.3	11.4	1.3	11.1	1.3
Am	Ag	34.2	2.8	28.0	2.4	29.6	2.6	31.6	2.7	28.7	3.0	21.9	2.0	18.1	1.8	<5.2		20.7	2.0
	Cd	5.0	1.5	<3.2		<3.2		<3.2		<5.0		<2.6		<2.8		<5.7		3.4	1.5
	Sn	117.8	8.5	60.4	4.8	66.9	5.2	51.7	4.2	78.5	6.4	63.8	4.8	52.7	4.2	<7.3		53.6	4.3
	Sb	4.5	2.2	<4.0		<4.8		<4.8		<6.9		4.6	2.0	<4.3		<7.9		<4.6	
	Te	<4.6		<5.3		<5.1		<5.3		<8.3		<4.3		<4.8		<9.1		<5.1	
	Cs	<6.6		<6.6		<6.6		<7.0		<9.7		<5.2		<5.9		<12.		<6.3	
	Ba	664.	47.	504.	36.	369.	26.	316.	23.	319.	23.	334.	24.	309.	22.	1299.	92.	345.	25.
	La	13.0	4.6	<9.8		<9.8		<9.7		<14.		<7.8		<8.7		51.9	9.3	<9.4	
	Ce	11.0	5.3	<11.		<10.		<11.		<16.		<9.1		<9.2		64.	11.	11.5	5.5

B-2. Trace Inorganic Components in Standards

SS	UNITS	EL	IAEA SOIL-5		1633A FLYASH		NBS COAL		306 SLUDGE EPA		IAEA SOIL-5	
TI				+/-		+/-		+/-		+/-		+/-
	%	AL	8.57	0.47	14.41	0.75	1.54	0.11	0.352	0.072	8.52	0.46
	%	SI	29.3	1.5	24.5	1.2	2.93	0.15	2.03	0.11	29.0	1.5
	%	P	<0.065		<0.058		0.078	0.013	0.845	0.050	<0.064	
	%	S	0.075	0.012	0.217	0.017	1.551	0.079	0.612	0.013	0.097	0.012
	%	CL	0.057	0.008	0.011		0.141	0.008	0.070	0.005	0.059	0.008
	%	K	2.39	0.12	2.27	0.12	0.321	0.016	0.150	0.008	2.37	0.12
	%	CA	2.64	0.13	1.231	0.062	0.399	0.020	1.979	0.099	2.60	0.13
ZR				+/-		+/-		+/-		+/-		+/-
	%	AL	7.62	0.79	13.02	0.96	1.80	0.39	1.80	0.49	7.82	0.80
	%	SI	26.7	1.4	22.5	1.2	2.77	0.23	2.06	0.25	26.6	1.4
	%	P	<0.37		<0.36		<0.14		0.78	0.11	<0.36	
	%	S	<0.16		0.199	0.081	1.390	0.084	0.480	0.052	<0.16	
	%	CL	0.078	0.034	<0.066		0.116	0.016	0.062	0.017	0.086	0.036
	%	K	1.837	0.095	1.671	0.087	0.293	0.016	0.149	0.010	1.863	0.097
	%	CA	2.32	0.12	1.024	0.054	0.458	0.024	2.43	0.12	2.33	0.12
	%	TI	0.472	0.024	0.753	0.038	0.107	0.006	0.106	0.006	0.469	0.024
	PPM	V	113.	25.	186.	31.	22.5	7.1	<17.		129.	25.
	PPM	CR	34.	13.	222.	20.	24.5	3.9	541.	29.	35.	13.
	PPM	MN	879.	47.	97.	15.	34.4	3.4	95.6	7.1	898.	48.
	%	FE	4.83	0.24	9.29	0.46	0.819	0.041	0.783	0.039	4.83	0.24
	PPM	NI	<10.		122.	10.	14.9	1.5	20.1	1.5	<10.	
	PPM	CU	79.4	4.7	119.2	6.9	16.2	1.1	309.	16.	82.8	4.9
	PPM	ZN	390.	20.	223.	12.	35.5	1.9	616.	31.	386.	20.
	PPM	GA	16.4	1.3	54.2	3.1	5.39	0.45	1.92	0.51	16.9	1.4
	PPM	SE	<0.96		9.44	0.85	2.40	0.32	2.29	0.33	<0.97	
	PPM	PB	151.5	8.0	69.3	4.1	7.54	0.91	58.8	3.2	153.9	8.1
	PPM	AS	97.6	5.3	144.2	7.5	5.07	0.49	<1.3		95.1	5.2
	PPM	BR	6.41	0.79	2.52	0.79	19.9	1.1	5.67	0.47	6.89	0.77
AG				+/-		+/-		+/-		+/-		+/-
	PPM	RB	131.7	9.3	140.3	10.0	21.2	1.7	3.67	0.73	130.9	9.3
	PPM	U	8.2	2.7	13.6	3.3	<2.8		10.3	1.4	<5.4	
	PPM	SR	363.	25.	842.	59.	159.	11.	87.5	6.2	361.	25.
	PPM	Y	24.7	1.9	92.0	6.6	10.42	0.94	3.00	0.68	25.8	2.
	PPM	ZR	258.	18.	331.	23.	38.6	2.8	802.	56.	259.	18.
	PPM	NB	9.7	0.97	29.7	2.3	3.95	0.64	<1.2		10.15	0.99
	PPM	MO	4.91	0.97	35.3	2.7	2.66	0.68	14.7	1.6	3.5	0.95
AM				+/-		+/-		+/-		+/-		+/-
	PPM	AG	4.6	1.8	6.3	1.8	<3.0		29.6	2.6	<3.4	
	PPM	CD	<3.7		<3.0		<3.3		<3.2		<3.7	
	PPM	SN	12.3	2.5	9.4	2.5	<4.3		66.9	5.2	10.9	2.4
	PPM	SB	15.9	2.9	9.9	2.9	<4.8		<4.8		20.6	3.0
	PPM	TE	<5.7		<5.7		7.3	2.0	<5.1		<5.4	
	PPM	CS	67.4	5.9	16.2	4.2	<7.4		<6.6		55.9	5.3
	PPM	BA	669.	47.	1500.	110.	310.	22.	369.	26.	614.	45.
	PPM	LA	34.6	5.5	98.6	8.9	15.4	5.2	<9.8		31.5	5.4
	PPM	CE	75.4	7.9	192.	15.	29.4	6.4	<10.		59.5	7.2

B-3. Inorganic Element Content of Product Oils

Run #		208		305		306		313		418		502-1		502-2		502-3A	
Source	Element		+/-		+/-		+/-		+/-		+/-		+/-		+/-		+/-
Ti	Al	1530.	270.	<2370.	400.	<2460.	300.	<1530.	290.	<4650.	530.	<1680.	350.	<1750.	340.	<2060.	340.
	Si	417.	98.	<2060.	210.	<530.	130.	<410.	110.	<280.	130.	<220.		<340.	110.	<320.	120.
	P	518.	82.	960.	120.	350.	100.	550.	87.	510.	120.	950.	120.	660.	100.	960.	120.
	S	5870.	310.	8550.	450.	6270.	330.	5830.	310.	9900.	520.	11140.	500.	8790.	460.	11950.	620.
	Cl	656.	44.	1860.	110.	22200.	1100.	247.	26.	6380.	330.	285.	32.	6630.	340.	563.	43.
	K	15.2	4.0	181.	13.	46.2	5.5	72.1	6.4	39.0	6.1	115.8	8.9	53.5	5.6	9.2	3.3
	Ca	163.4	9.7	1604.	82.	411.	22.	372.	20.	84.8	6.8	52.8	4.6	41.5	3.9	21.9	3.0
Zr	Ti	43.4	5.1	114.	10.	36.9	5.3	35.2	4.7	41.4	8.3	24.4	6.7	20.2	5.4	<8.6	
	V	10.2	3.0	16.6	4.8	13.4	3.1	12.5	2.7	22.2	5.1	27.6	4.6	17.8	3.7	9.2	3.0
	Cr	11.3	2.4	46.7	4.5	19.5	2.7	16.3	2.2	13.9	3.6	11.7	3.1	8.2	2.6	6.2	2.3
	Mn	3.5	1.5	12.1	2.4	<2.9		2.7	1.2	<4.0		<3.6		4.0	1.5	5.9	1.4
	Fe	561.	29.	1966.	99.	777.	39.	478.	24.	782.	40.	352.	18.	137.1	7.3	78.6	4.5
	Co	<4.7		<5.5		<3.8		<2.8		4.1	2.1	<2.6		<1.8		<1.6	
	Ni	14.1	1.4	19.2	1.4	9.31	0.04	8.29	0.74	9.60	0.99	8.00	0.81	5.49	0.64	3.46	0.59
	Cu	48.4	3.0	111.7	5.8	15.3	1.1	13.01	0.90	6.61	0.71	6.32	0.63	5.94	0.57	3.75	0.52
	Zn	108.1	5.9	182.9	9.3	43.6	2.4	41.9	2.2	59.0	3.1	17.3	1.0	20.1	1.1	5.31	0.49
	Ga	<0.86		<0.65		<0.57		<0.42		<0.57		<0.48		<0.46		<0.48	
	Hg	<3.4		2.9	1.2	<2.3		1.81	0.90	<2.3		<2.1		2.3	1.0	<2.1	
	Se	1.23	0.50	1.63	0.29	1.62	0.32	0.91	0.25	1.01	0.29	1.28	0.25	1.97	0.27	2.26	0.32
	Pb	7.8	1.5	17.9	1.3	1.96	0.96	4.71	0.78	<1.6		2.13	0.70	1.64	0.72	<1.6	
	As	<1.1		<0.86		1.41	0.39	<0.58		0.91	0.35	0.62	0.30	0.67	0.30	<0.62	
	Br	1.84	0.46	2.46	0.31	1.43	0.32	2.43	0.28	1.44	0.29	2.42	0.27	1.85	0.26	1.80	0.30
	Rb	<1.0		<0.55		<0.66		<0.54		<0.57		<0.46		<0.50			
	Sr	<7.5		<4.0		<4.9		<4.2		<4.4		<3.5		<3.8		<4.3	
Ag	U	<3.4		<2.0		<2.3		<1.6		1.34	0.39	<1.6		<1.7		<2.1	
	Sr	<1.6		8.82	0.79	1.96	0.54	1.79	0.42	<0.86		<0.76		<0.76		<0.97	
	Y	<1.9		<1.0		<1.2		<0.85		6.28	0.64	<0.85		<0.90		<1.1	
	Zr	<2.0		60.6	4.3	7.93	0.87	39.5	2.9	<0.89		9.04	0.80	12.7	1.0	6.75	0.76
	Nb	<2.1		<1.0		<1.3		<1.00		2.42	0.53	<0.92		1.08	0.47	<1.2	
	Mo	7.6	1.3	10.88	0.99	9.08	0.96	7.91	0.82		<1.2	16.5	1.3	8.75	0.80	12.7	1.1
Am	Ru	<3.0		<1.8		<2.4		<1.8		<3.4		<1.6		<2.6		<1.8	
	Rh	<3.4		<2.0		<2.6		<2.0		<3.6		<1.7		<2.7		<2.0	
	Pd	<4.0		<2.3		3.1	1.5	<2.4		7.3	1.9	<2.0		<3.0		2.8	1.2
	Ag	<4.6		7.8	1.4	<3.5		<2.7		4.2	2.1	<2.2		<3.3		<2.7	
	Cd	<5.0		<2.7		<3.6		<2.8		<4.7		<2.3		<3.3		<2.8	
	In	<5.4		<2.8		<3.8		<3.0		4.8	2.4	<2.4		<3.5		<3.0	
	Sn	33.7	4.0	47.6	3.7	9.0	2.3	28.8	2.7	37.3	3.8	27.2	2.4	30.1	2.9	12.5	2.0
	Sb	<7.2		<3.7		5.3	2.6	<4.1		<5.5		<3.1		<4.3		<4.1	
	Te	<8.2		<4.0		<5.7		<4.4		<6.9		<3.3		<4.5		<4.2	
	I	<9.9		<4.7		<6.7		<5.2		<7.5		<4.0		<5.5		<5.3	
	Cs	<11.		<5.2		<7.4		<5.8		<7.6		<4.2		<5.5		<5.5	
	Ba	<12.		46.5	4.4	14.1	4.2	27.3	3.8	13.1	4.5	5.7	2.5	7.2	3.3	<6.5	
	La	<15.		9.1	3.7	<10.		9.1	4.1	<11.		<6.3		<8.3		<8.3	
	Ce	<16.		<7.7		<12.		<9.5		<14.		<6.7		<9.5		<8.8	

Inorganic Element Content of Product Oils (continued)

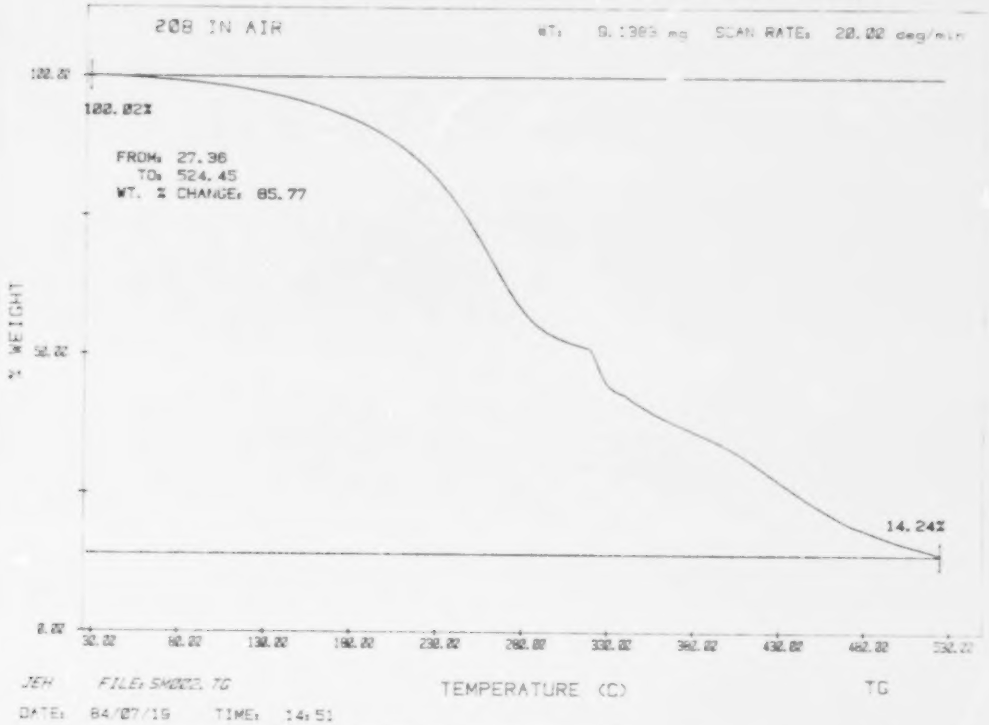
	507-4		507-5		507-6		509-6		509-7A		509-7B		NBS 1634A Fuel Oil	
		+/-		+/-		+/-		+/-		+/-		+/-		+/-
Al	<2050.	360.	<1640.	340.	<2040.	410.	<2860.	390.	<1950.	360.	<1920.	320.	<2430.	370.
Si	1330.	150.	1770.	190.	620.	140.	260.	120.	2180.	190.	390.	110.	<250.	
P	690.	100.	770.	110.	<220.		750.	110.	232.	90.	1000.	110.	2490.	200.
S	8950.	470.	10680.	550.	5710.	310.	9830.	510.	5450.	290.	11270.	580.	31000.	1600.
Cl	2330.	130.	2700.	150.	35700.	1800.	6980.	360.	18280.	920.	1024.	64.	<64.	
K	128.9	9.4	81.6	7.1	42.4	5.2	64.8	5.7	59.3	5.6	7.5	2.9	<5.1	
Ca	40.7	4.0	41.2	4.0	21.5	3.0	25.2	3.1	20.1	2.9	45.0	4.0	22.2	3.1
Ti	16.7	5.3	25.7	6.0	59.8	7.1	13.3	4.7	17.8	4.9	<7.3		<9.0	
V	19.5	3.5	18.9	3.9	12.4	3.8	7.5	3.1	9.3	3.2	7.7	2.8	54.7	4.9
Cr	<4.8		7.6	2.7	13.1	2.8	9.4	2.2	<4.6		<4.5		<4.5	
Mn	5.7	1.5	<3.1		<3.1		3.3	1.3	2.9	1.4	<3.2		<2.7	
Fe	135.4	7.2	321.	17.	269.	14.	114.3	6.2	130.6	7.0	58.2	4.1	31.9	2.2
Co	<1.8		<2.4		<2.3		<1.7		<1.8		<2.3		<1.5	
Ni	4.94	0.61	6.30	0.70	6.77	0.73	5.25	0.61	5.53	0.64	3.93	0.93	30.2	1.8
Cu	4.00	0.50	3.89	0.51	2.51	0.53	6.63	0.61	4.26	0.54	<1.5		<0.97	
Zn	10.98	0.72	5.55	0.47	6.57	0.52	12.14	0.76	9.03	0.64	13.4	1.1	2.84	0.39
Ga	<0.44		<0.43		<0.46		<0.41		<0.47		<0.81		<0.51	
Hg	<1.8		<2.0		<2.0		<1.8		<2.0		5.8	2.1	<2.1	
Se	1.94	0.25	1.61	0.25	1.17	0.26	1.84	0.26	0.85	0.26	1.09	0.54	<0.58	
Pb	<1.4		<1.4		<1.4		<1.4		<1.5		<3.0		2.86	0.88
As	<0.55		<0.45		<0.58		0.64	0.20	<0.60		1.51	0.46	<0.69	
Br	1.94	0.26	2.94	0.29	0.89	0.24	0.96	0.23	1.10	0.26	2.13	0.56	<0.53	
Rb	<0.47		<0.46		<0.49		<0.49		<0.54		<1.1		<0.61	
Sr	<3.6		<3.6		<3.8		<3.8		<4.2		<7.8		<4.5	
U	<1.6		<1.6		<1.7		<1.5		<1.8		<4.1		<2.1	
Sr	0.84	0.39	0.81	0.38	<0.79		<0.72		<0.83		<1.8		1.08	0.48
Y	<0.84		<0.84		<0.88		<0.80		<0.93		<2.0		<1.1	
Zr	13.2	1.1	7.72	0.71	4.55	0.57	1.93	0.46	7.31	0.76	6.2	1.2	<1.1	
Nb	<0.95		<0.92		<0.97		<0.92		<1.1		<2.2		<1.2	
Mo	6.69	0.69	4.40	0.59	2.57	0.55	8.07	0.75	3.13	0.60	<2.5		<1.2	
Ru	<2.0		<1.7		<1.8		<2.0		<3.1		<3.3		<2.0	
Rh	<2.1		<1.8		<1.9		<2.2		<3.3		<3.8		<2.2	
Pd	<2.4		3.0	1.1	<2.3		3.2	1.3	<3.6		<4.5		<3.3	1.3
Ag	<2.6		<2.4		<2.6		<2.8		<3.9		<5.0		<3.0	
Cd	<2.7		<2.4		<2.7		<2.9		<4.0		<5.5		<3.2	
In	<2.9		<2.5		<2.7		<3.0		<4.1		<5.9		<3.3	
Sn	16.7	2.0	15.3	1.8	16.3	1.9	6.1	1.8	21.0	2.7	8.4	3.6	<3.9	
Sb	<3.8		<3.4		<3.7		<4.0		<5.1		<7.8		<4.4	
Te	<4.1		<3.4		<4.0		<4.3		<5.3		<9.2		<4.9	
I	<4.8		<4.3		5.5	2.4	<5.0		<6.4		<11.		<5.9	
Cs	<5.3		<4.7		<4.9		<5.5		<6.4		<11.		<6.5	
Ba	11.4	3.0	<5.1		<5.8		7.3	3.1	<7.7		<13.		<7.3	
La	7.8	3.7	<6.5		<7.3		<7.7		11.4	4.9	<17.		<9.2	
Ce	<8.5		<7.7		<7.8		<8.9		<11.		<20.		<9.7	

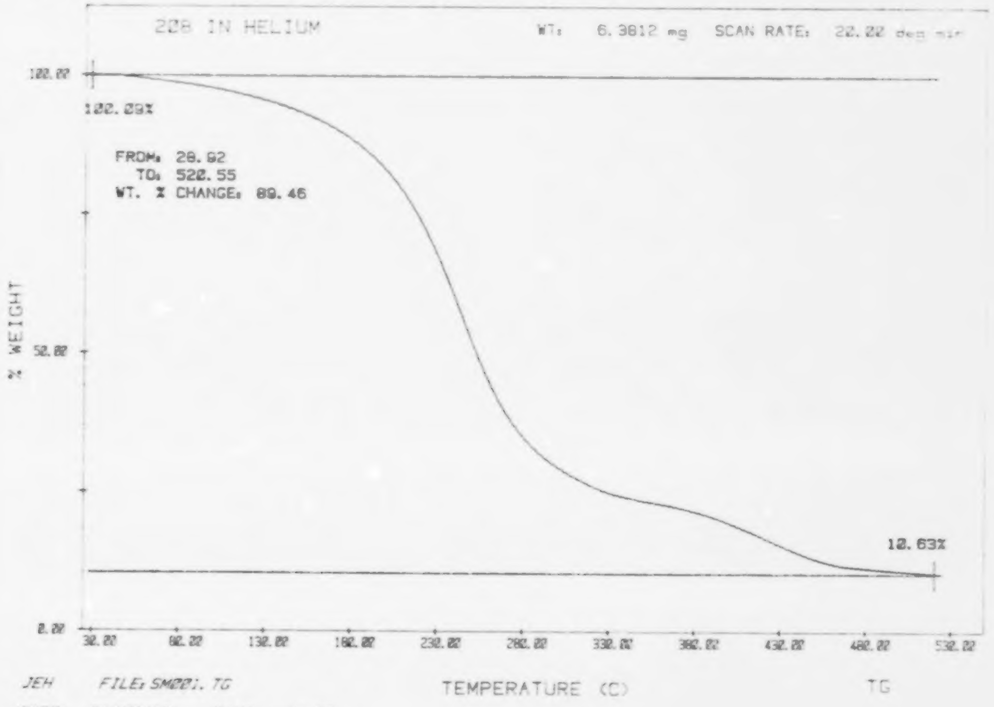
B-4. Trace Inorganic Components in Chars

Source	Element	Run # 208		305		306		313		418		IAEA SOIL-5	
Zr	V	<47.		<55.		<72.		<37.		<21.		129.	25.
	Cr	603.	34.	1398.	74.	1107.	65.	719.	39.	220.	14.	35.	13.
	Mn	460.	26.	564.	33.	451.	32.	331.	20.	112.0	8.1	898.	48.
	Ni	159.0	9.5	432.	23.	308.	18.	267.	14.	73.1	4.7	<10.	
	Cu	4160.	210.	3430.	170.	2100.	110.	2130.	110.	785.	40.	82.8	4.9
	Zn	3970.	200.	4080.	200.	2500.	130.	3000.	150.	1347.	68.	386.	20.
	Ga	15.7	2.0	13.4	2.1	10.8	2.3	7.6	1.5	5.2	1.0	16.8	1.4
	Se	10.76	0.87	14.7	1.1	11.4	1.1	12.72	0.90	5.89	0.67	<0.97	
	Pb	618.	31.	509.	26.	322.	17.	469.	24.	156.9	0.67	153.9	8.1
	As	<5.0		<5.3		<5.7		<4.2		<2.8		95.1	5.2
	Br	2.36	0.51	3.68	0.61	1.60	0.68	4.26	0.51	12.68	0.91	6.89	0.77
Ag	Rb	5.1	1.1	13.4	1.6	16.7	1.7	6.4	1.1	5.99	0.66	130.9	9.3
	U	25.7	2.5	36.3	3.5	30.3	3.0	19.2	2.2	12.8	2.0	<5.4	
	Sr	369.	26.	396.	28.	379.	27.	239.	17.	129.5	9.2	361.	25.
	Y	8.7	1.1	10.7	1.4	13.4	1.4	9.6	1.3	<2.0		25.8	2.0
	Zr	607.	43.	2240.	160.	2610.	180.	3160.	220.	1227.	86.	259.	18.
	Nb	4.61	0.71	4.76	0.93	5.25	0.85	3.23	0.78	1.94	0.85	10.15	0.99
	Mo	72.7	5.2	140.	10.	160.	11.	116.9	8.5	34.6	3.1	3.50	0.95
Am	Ag	166.	12.	161.	11.	165.	12.	187.	13.	70.2	5.9	<3.4	
	Cd	18.6	2.0	15.8	2.2	15.2	1.9	15.9	2.0	<7.0		<3.7	
	Sn	513.	36.	367.	26.	229.	16.	329.	23.			10.9	2.4
	Sb	17.5	2.5	14.2	2.8	11.2	2.4	13.3	2.6	130.	10.	20.6	3.0
	Te	<4.6		<5.3		<4.4		<5.1		<11.		<5.4	
	Cs	<6.0		<7.7		<6.3		<6.5		<14.		55.9	5.3
	Ba	1790.	130.	920.	140.	1900.	130.	1215.	85.	520.	38.	644.	45.
	La	11.8	4.4	19.2	5.4	10.5	4.3	15.8	4.9	<20.		31.5	5.4
	Ce	29.1	5.4	23.2	6.3	20.7	5.1	27.7	5.8	<23.		59.5	7.2

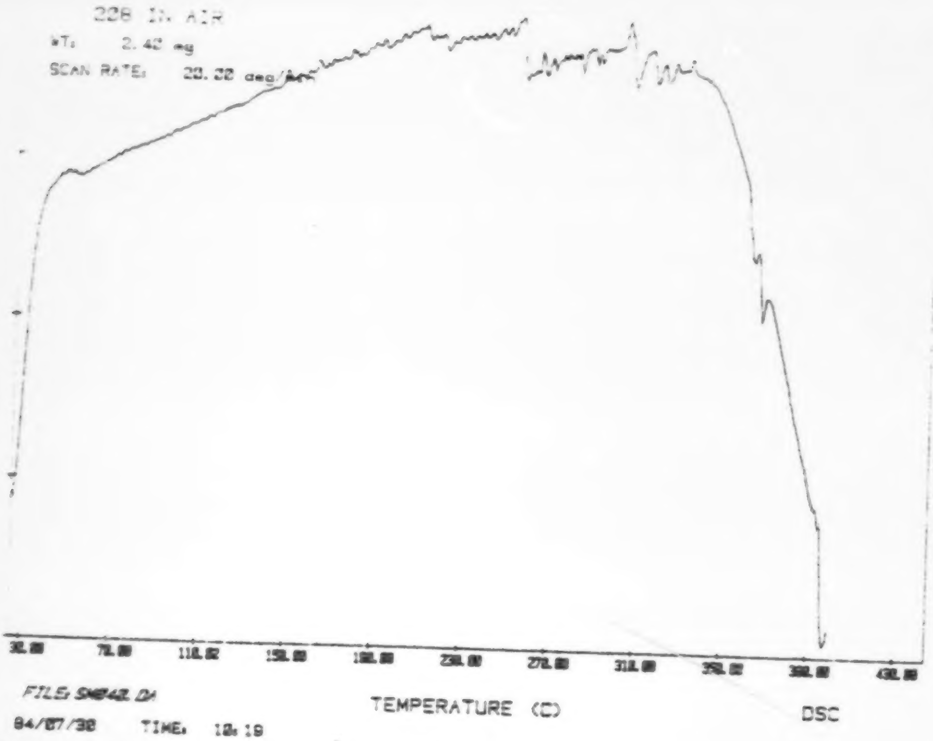
APPENDIX C

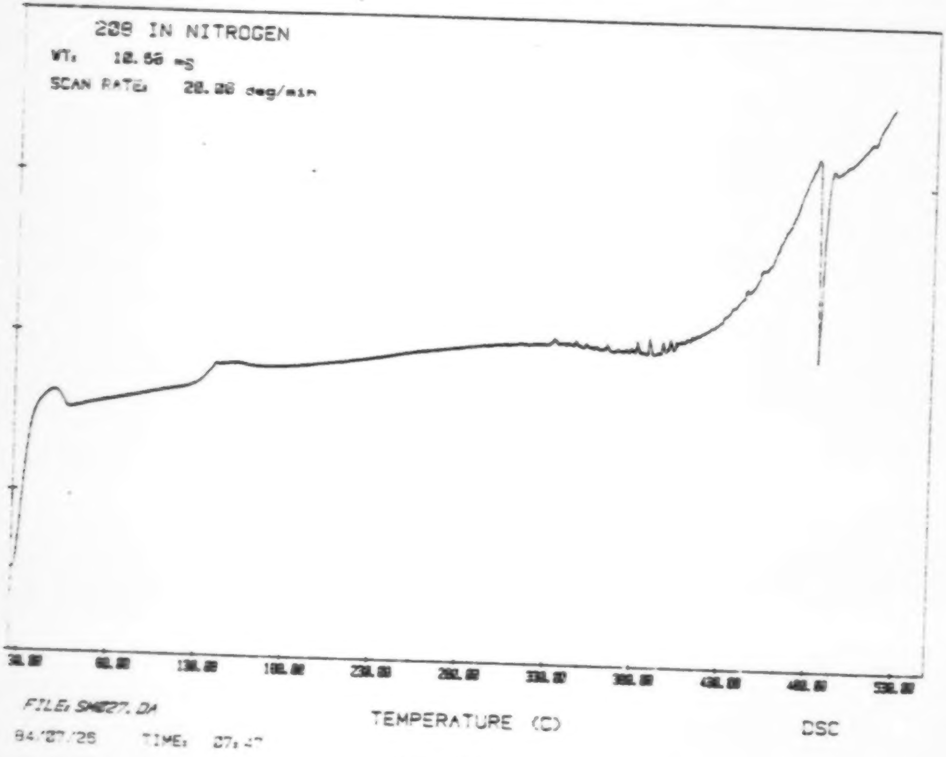
Oil Thermal Analysis Profiles (TG and DCS)



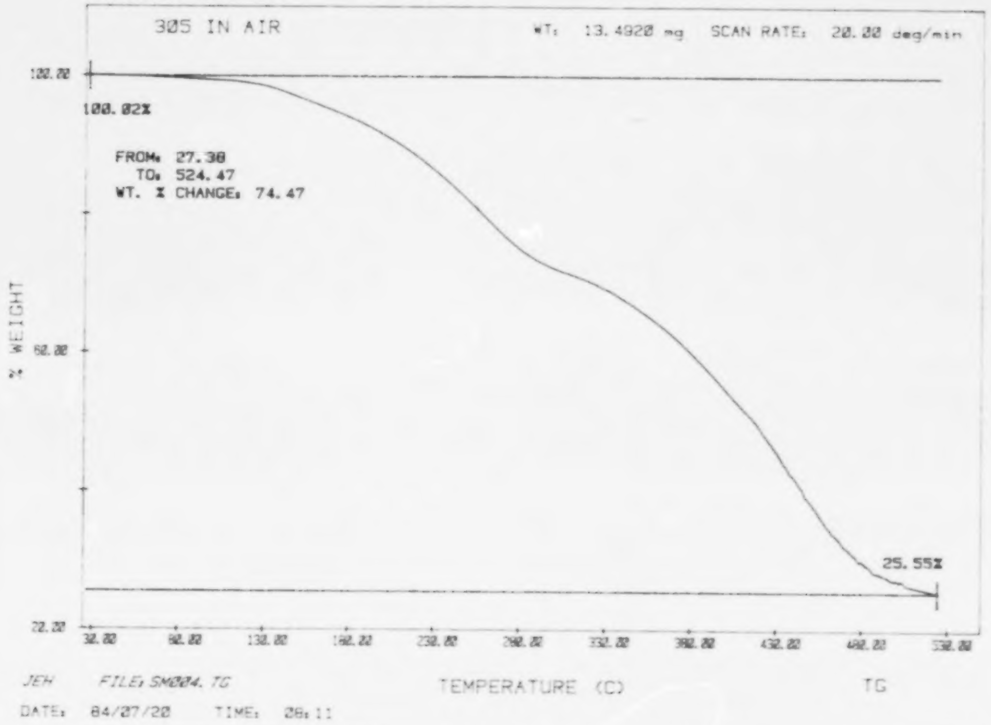


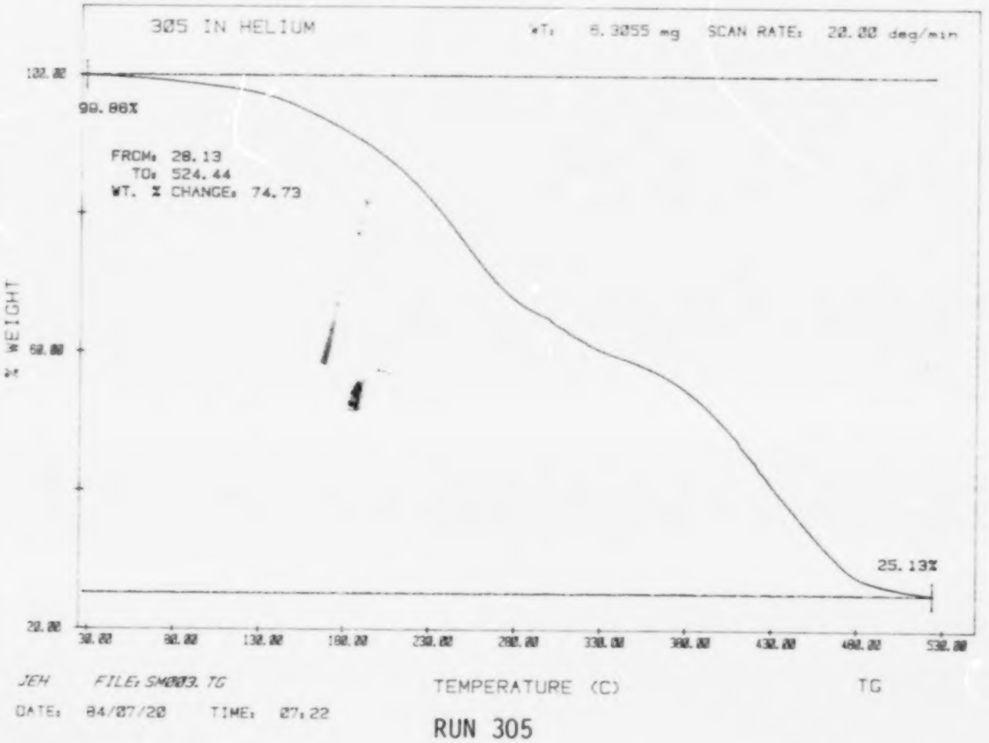
RUN 208


208 IN AIR
WT: 2.40 mg
SCAN RATE: 20.00 deg/min
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
FILE: SM042.DA
TEMPERATURE (C)
DSC
84/07/30 TIME: 10:19

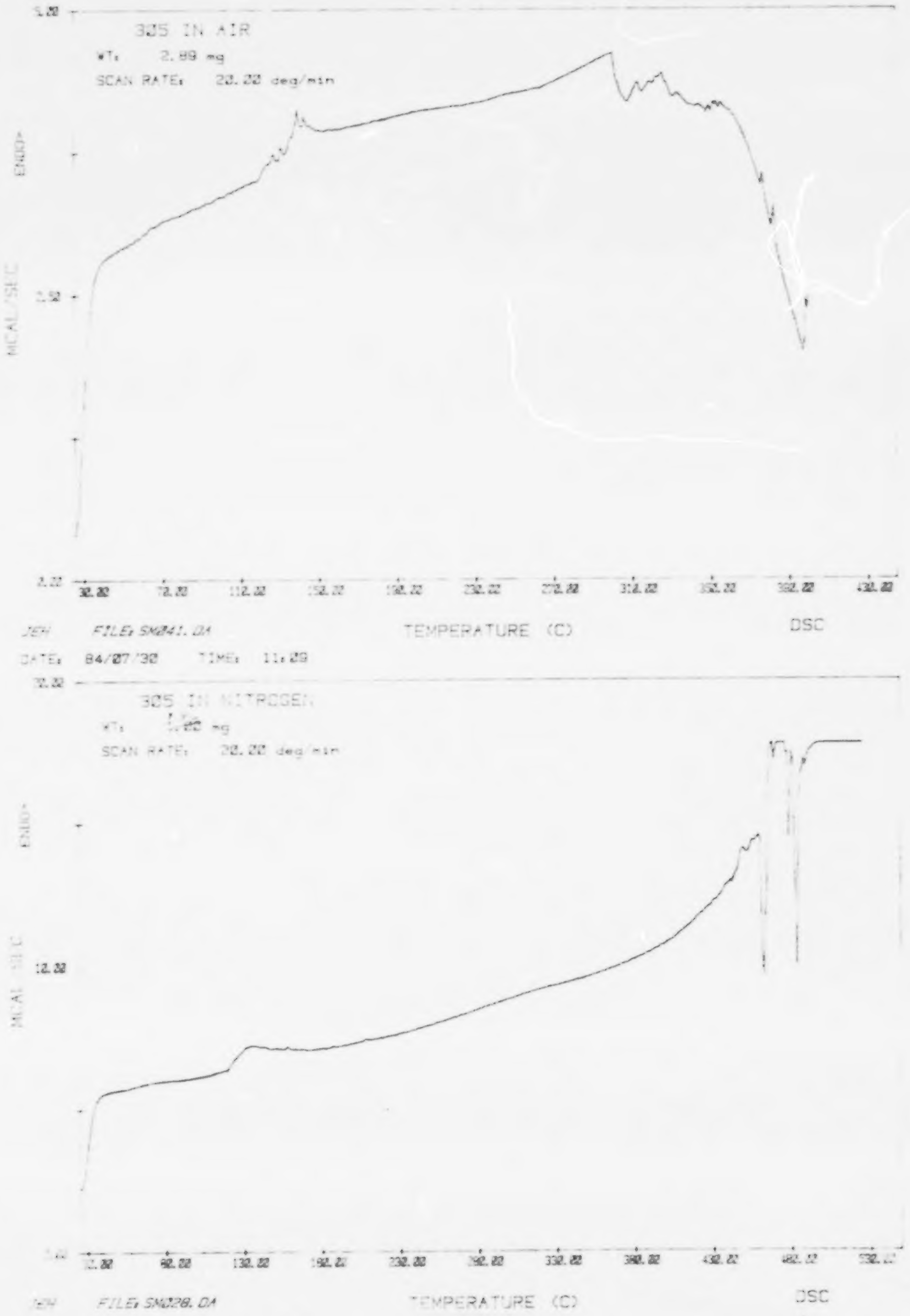

208 IN NITROGEN
WT: 10.56 mg
SCAN RATE: 20.00 deg/min
30.00
80.00
130.00
180.00
230.00
280.00
330.00
380.00
430.00
480.00
530.00
FILE: SM027.DA
TEMPERATURE (C)
DSC
84/07/26 TIME: 07:47

RUN 208

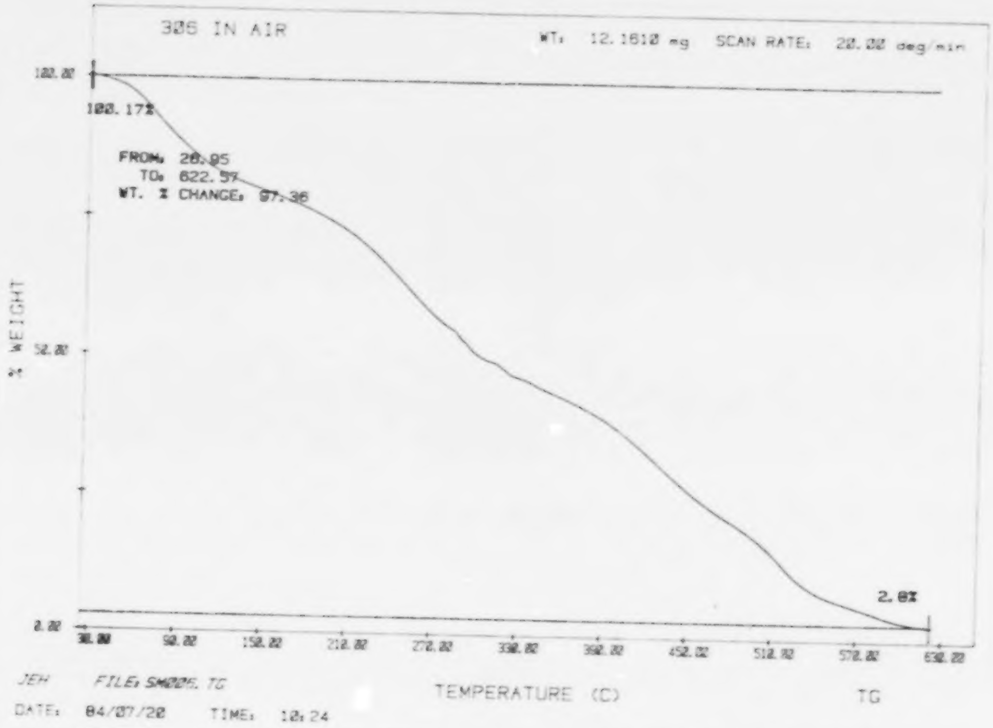

305 IN AIR
WT: 13.4920 mg SCAN RATE: 20.00 deg/min
100.02%
FROM: 27.30
TO: 524.47
WT. % CHANGE: 74.47
25.55%
% WEIGHT
100.00
60.00
20.00
30.00
80.00
130.00
180.00
230.00
280.00
330.00
380.00
430.00
480.00
530.00
TEMPERATURE (C)
TG
JEH FILE: SM004.TG
DATE: 84/07/20 TIME: 08:11

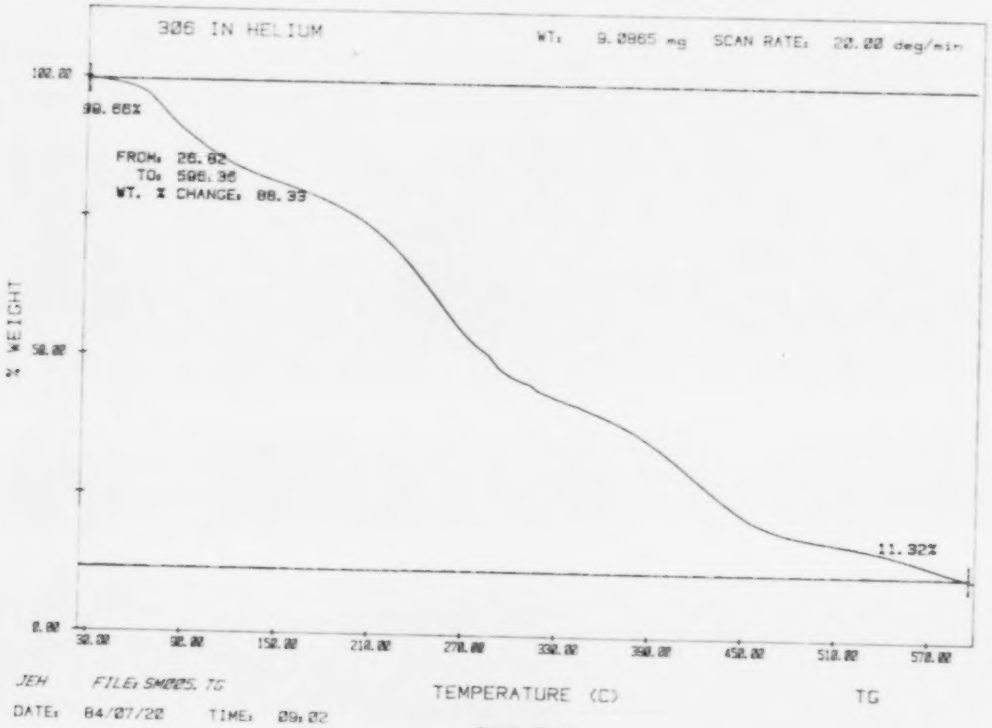

305 IN HELIUM
WT: 6.3055 mg SCAN RATE: 20.00 deg/min
99.86%
FROM: 28.13
TO: 524.44
WT. % CHANGE: 74.73
25.13%
% WEIGHT
100.00
60.00
20.00
30.00
80.00
130.00
180.00
230.00
280.00
330.00
380.00
430.00
480.00
530.00
TEMPERATURE (C)
TG
JEH FILE: SM003.TG
DATE: 84/07/20 TIME: 07:22

RUN 305

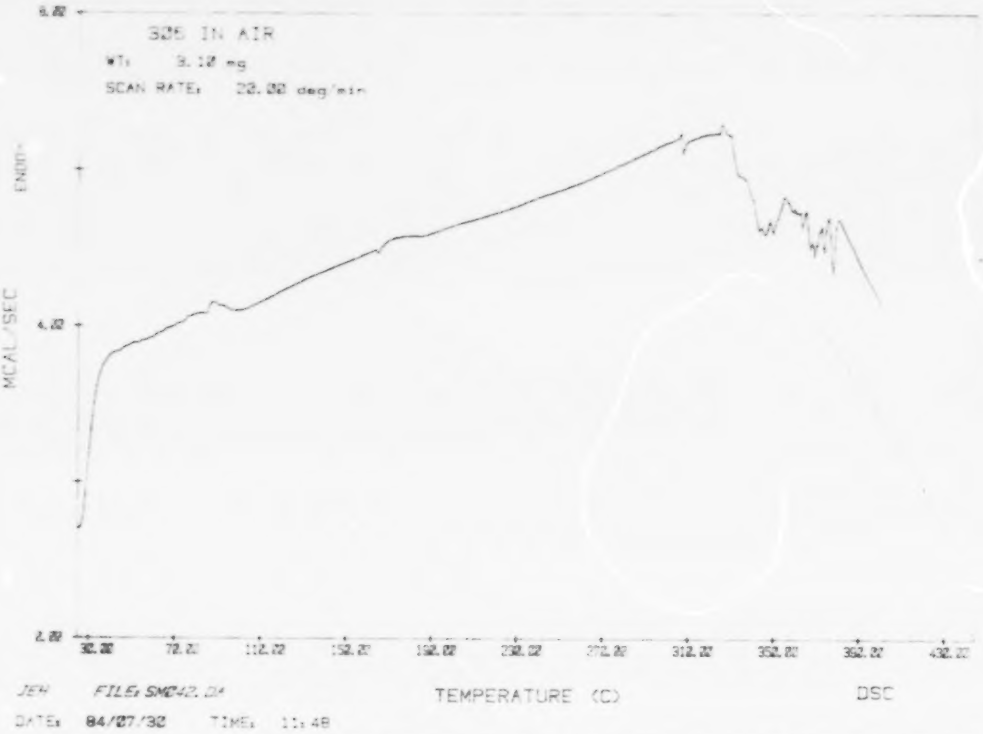

5.00
305 IN AIR
WT: 2.89 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
2.50
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM041.DA
TEMPERATURE (C)
DSC
DATE: 84/07/30 TIME: 11:29
20.00
305 IN NITROGEN
WT: 1.00 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
10.00
0.00
30.00
80.00
130.00
180.00
230.00
280.00
330.00
380.00
430.00
480.00
530.00
JEH FILE: SM028.DA
TEMPERATURE (C)
DSC
DATE: 84/07/26 TIME: 20:32

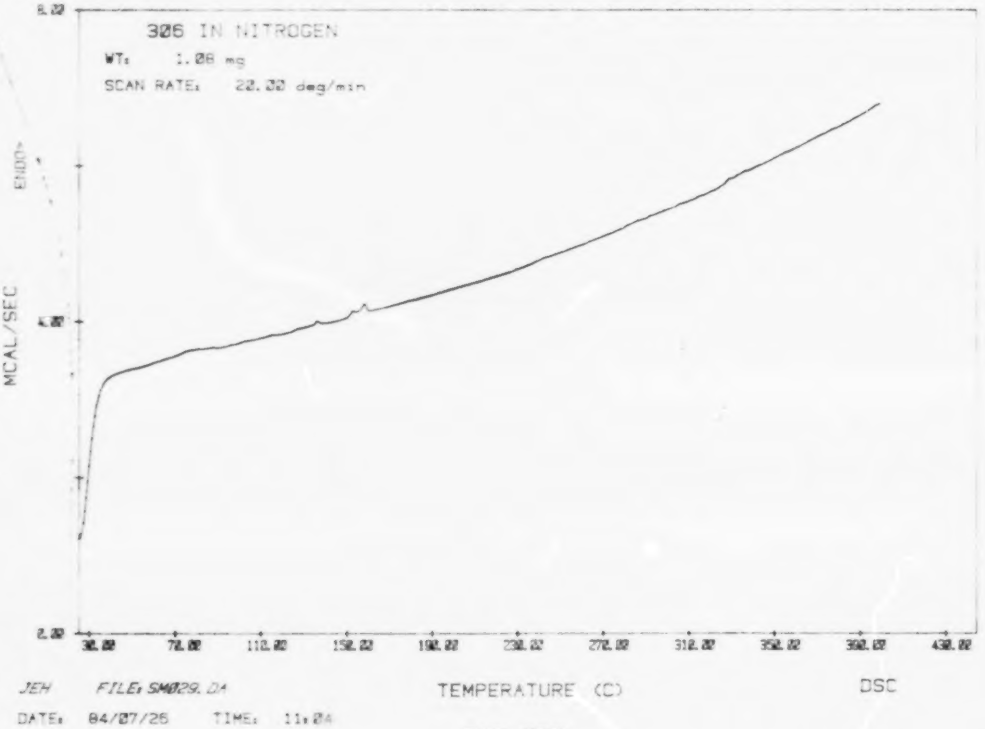
RUN 305


306 IN AIR
WT: 12.1610 mg SCAN RATE: 20.00 deg/min
100.00
100.17%
FROM: 20.95
TO: 622.57
WT. % CHANGE: 97.36
% WEIGHT
50.00
2.8%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM005.TG
TEMPERATURE (C)
TG
DATE: 84/07/20 TIME: 10:24

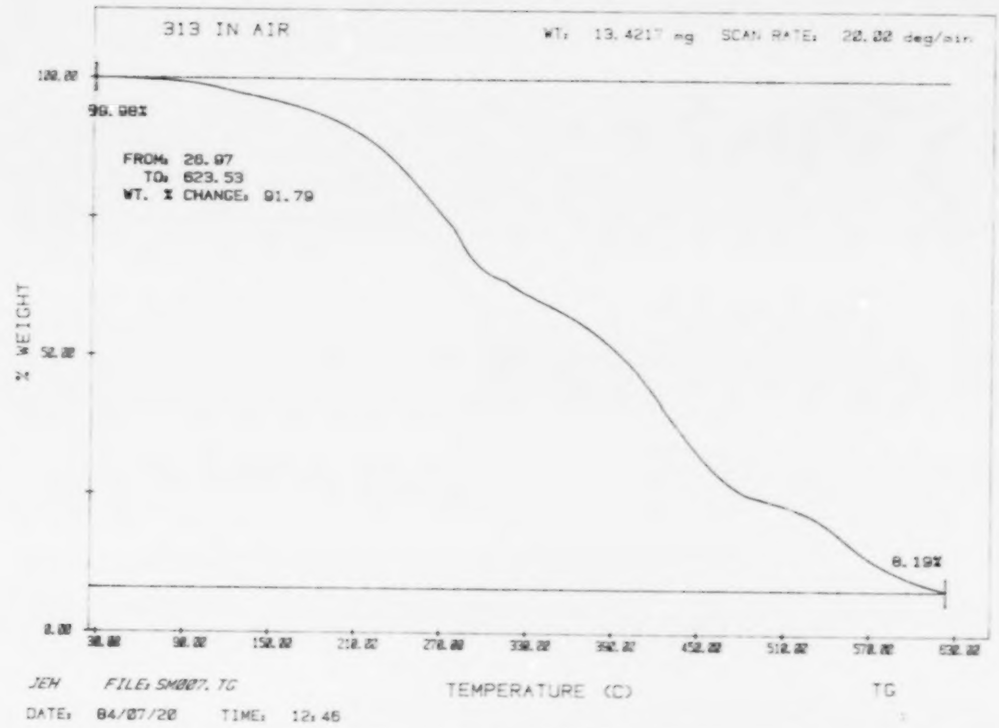

306 IN HELIUM
WT: 9.0865 mg SCAN RATE: 20.00 deg/min
100.00
99.66%
FROM: 26.82
TO: 595.36
WT. % CHANGE: 88.33
% WEIGHT
50.00
11.32%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
JEH FILE: SM005.TG
TEMPERATURE (C)
TG
DATE: 84/07/20 TIME: 09:02

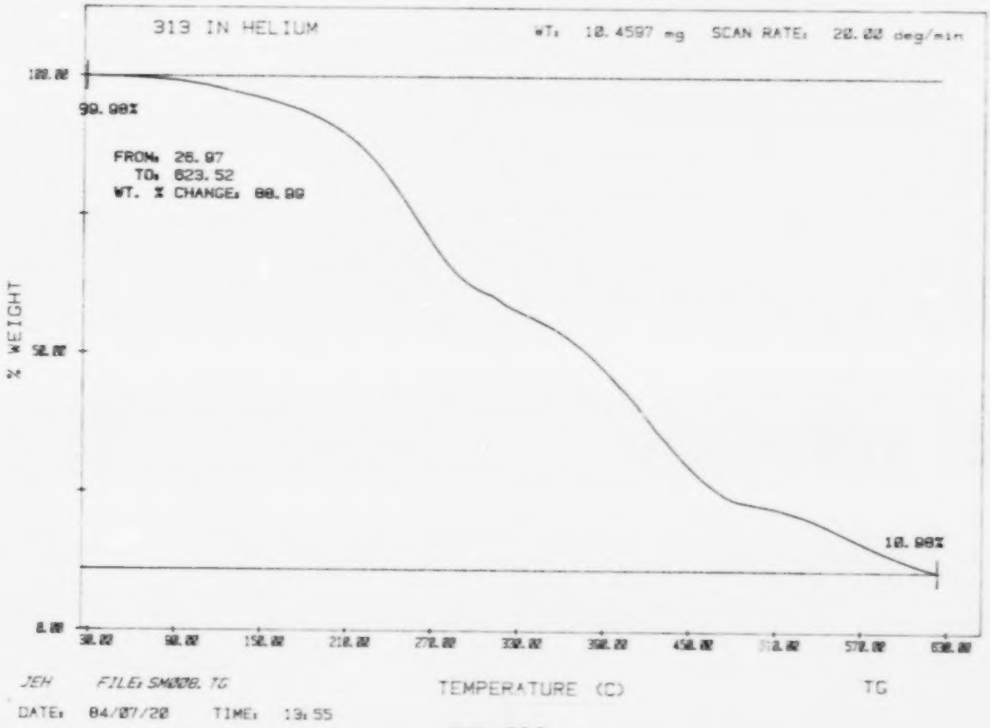
RUN 306


306 IN AIR
WT: 3.10 mg
SCAN RATE: 20.00 deg/min
6.00
4.00
2.00
ENDO>
MCAL/SEC
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
JEH FILE: SM042.DA
DATE: 84/07/30 TIME: 11:48

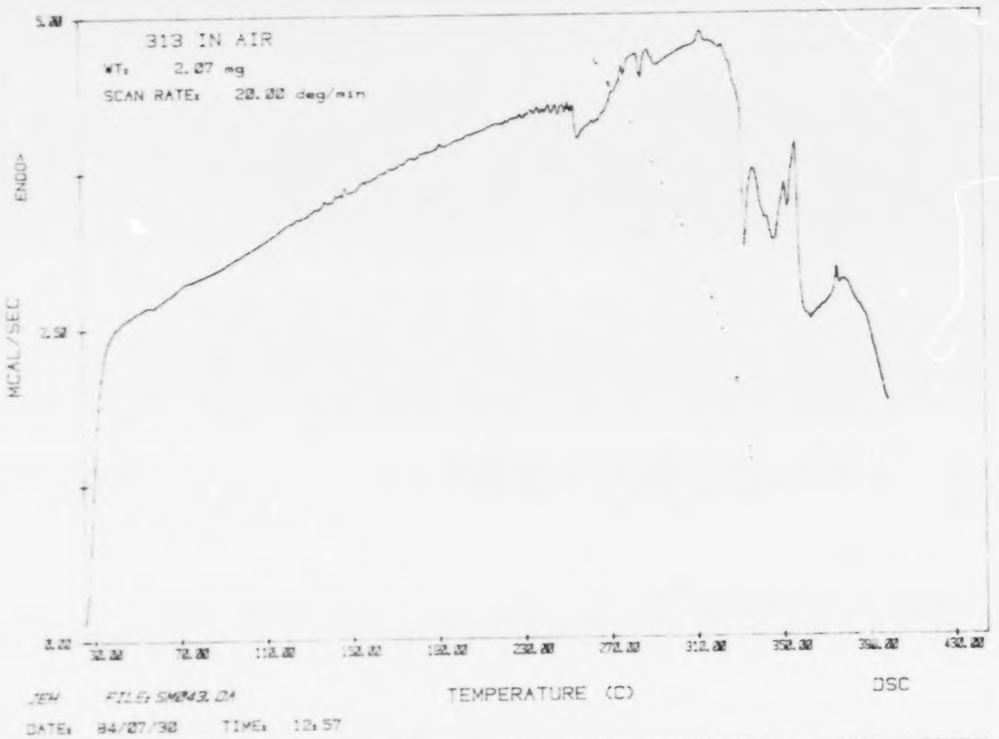

306 IN NITROGEN
WT: 1.08 mg
SCAN RATE: 20.00 deg/min
6.00
4.00
2.00
ENDO>
MCAL/SEC
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
JEH FILE: SM029.DA
DATE: 84/07/26 TIME: 11:04

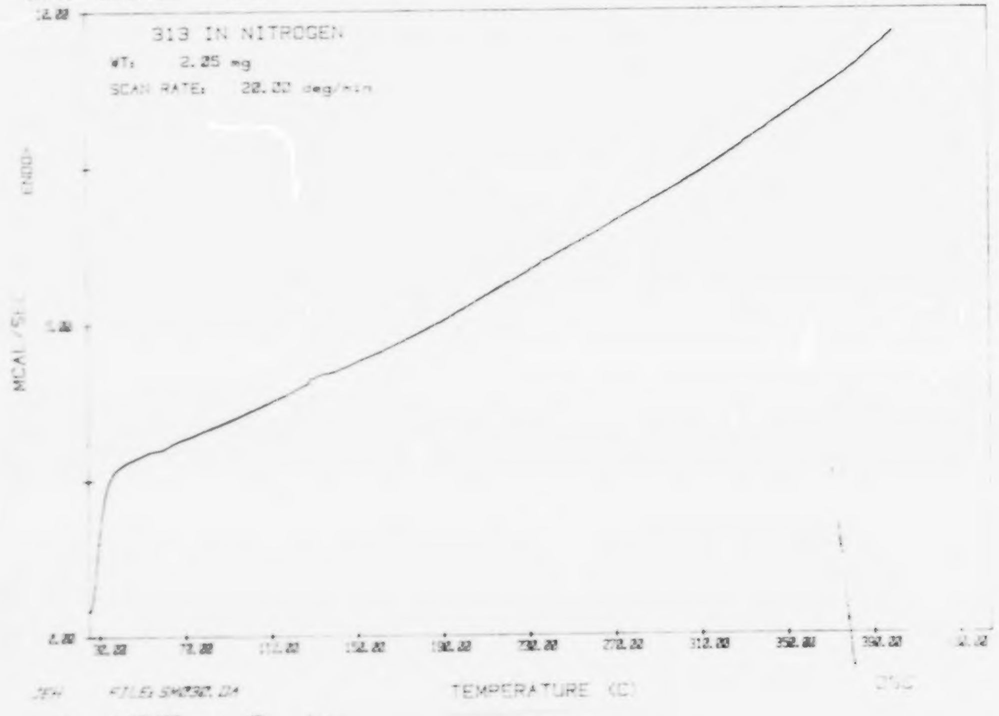
RUN 306


313 IN AIR
WT: 13.4217 mg SCAN RATE: 20.00 deg/min
100.00
99.98%
FROM: 26.97
TO: 623.53
WT. % CHANGE: 91.79
% WEIGHT
50.00
8.19%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
TEMPERATURE (C)
TG
JEH FILE: SM007.TG
DATE: 84/07/20 TIME: 12:46

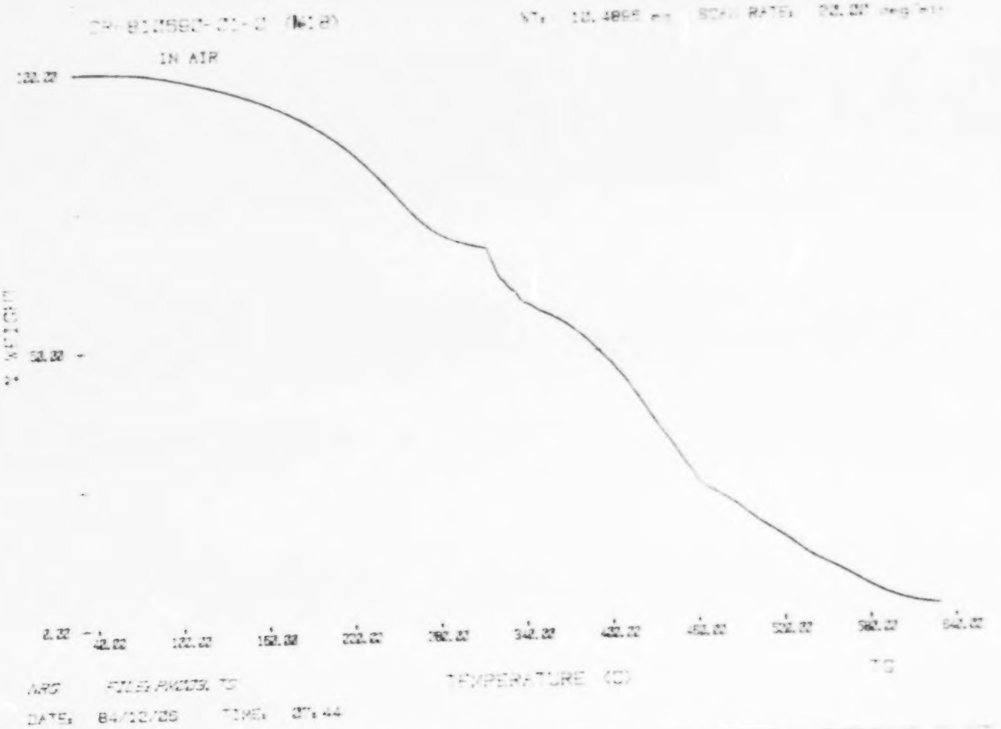

313 IN HELIUM
WT: 10.4597 mg SCAN RATE: 20.00 deg/min
100.00
99.98%
FROM: 26.97
TO: 623.52
WT. % CHANGE: 88.99
% WEIGHT
50.00
10.98%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
TEMPERATURE (C)
TG
JEH FILE: SM008.TG
DATE: 84/07/20 TIME: 13:55

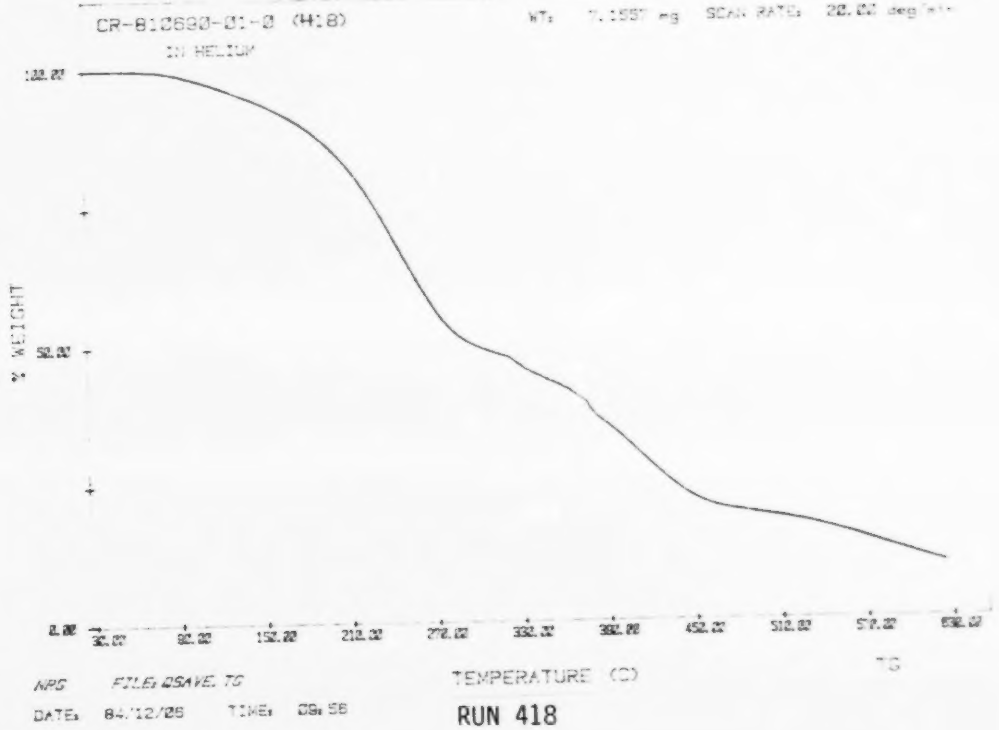
RUN 313


5.00
2.50
0.00
313 IN AIR
WT: 2.07 mg
SCAN RATE: 20.00 deg/min
MCAL/SEC ENDO>
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM043.DA
TEMPERATURE (C)
DSC
DATE: 84/07/30 TIME: 12:57

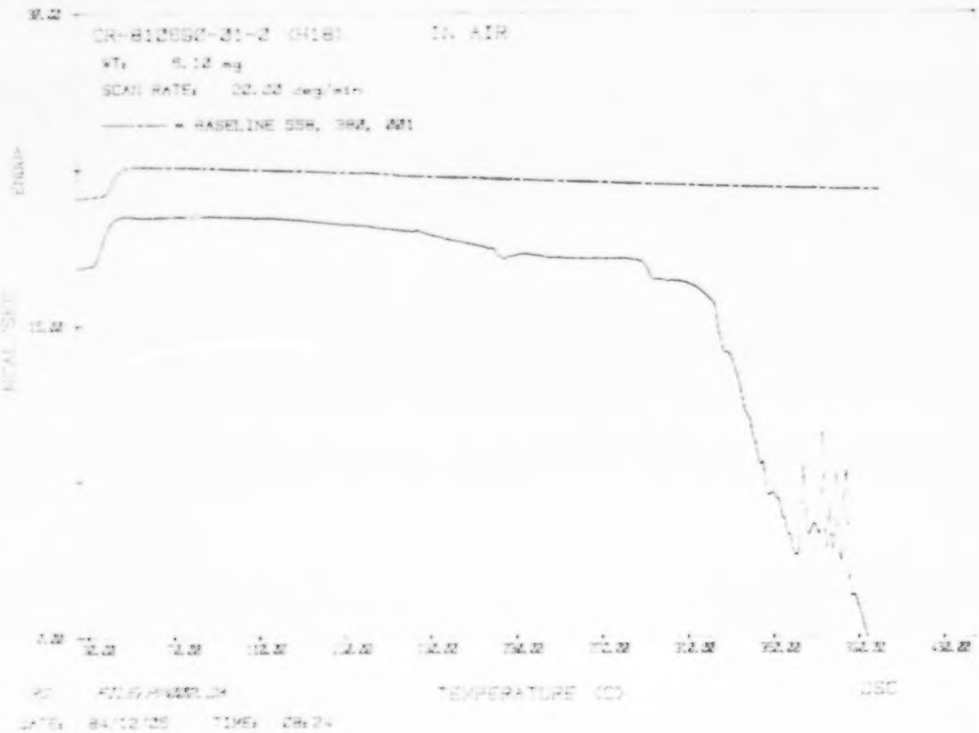

10.00
5.00
0.00
313 IN NITROGEN
WT: 2.05 mg
SCAN RATE: 20.00 deg/min
MCAL/SEC ENDO>
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM030.DA
TEMPERATURE (C)
DSC

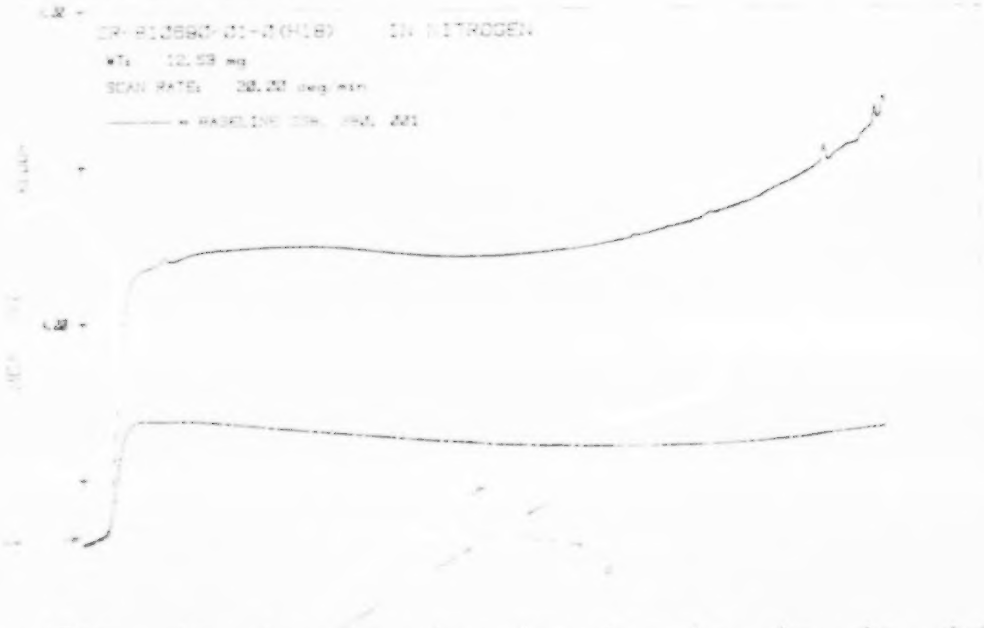
RUN 313


CR-810690-01-0 (H18)
IN AIR
WT: 10.4895 mg SCAN RATE: 20.00 deg/min
100.00
50.00
0.00
% WEIGHT
40.00
100.00
160.00
220.00
280.00
340.00
400.00
460.00
520.00
580.00
640.00
TEMPERATURE (C)
TG
NRS FILE: PK0039.TG
DATE: 84/12/06 TIME: 07:44

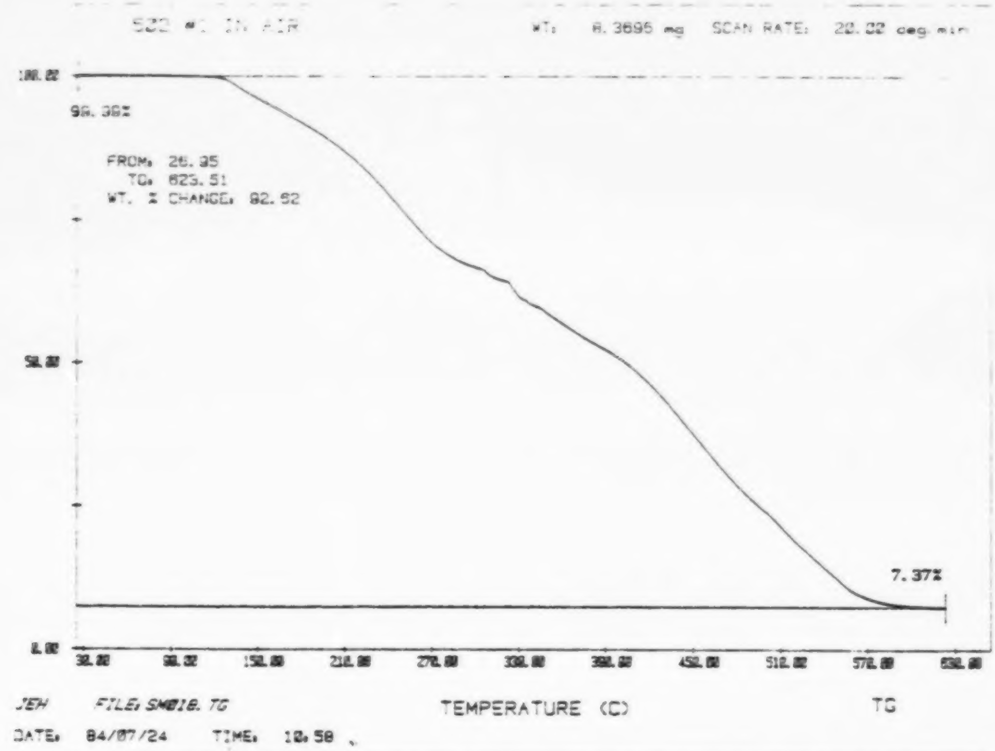

CR-810690-01-0 (H18)
IN HELIUM
WT: 7.1557 mg SCAN RATE: 20.00 deg/min
100.00
50.00
0.00
% WEIGHT
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
TEMPERATURE (C)
TG
NRS FILE: QSAVE.TG
DATE: 84/12/06 TIME: 09:56

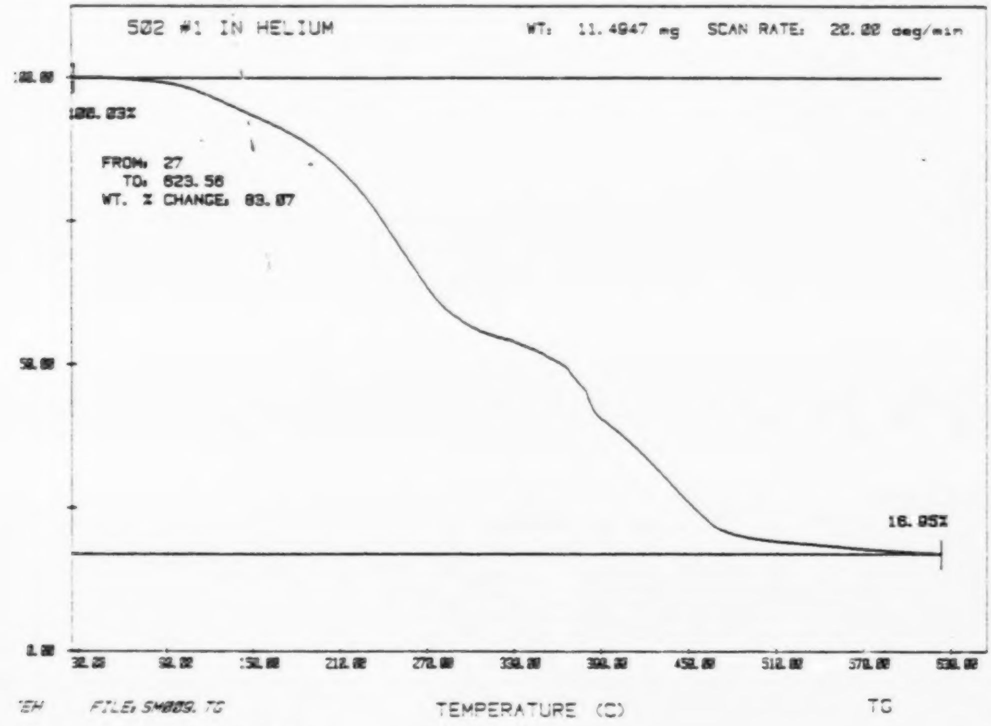
RUN 418


30.00
CR-812880-01-2 (H18)
IN AIR
WT: 9.12 mg
SCAN RATE: 20.00 deg/min
= BASELINE 558, 300, 001
ENDO
MCAL/SEC
15.00
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
DATE: 84/12/05
TIME: 08:24


8.00
CR-812880-01-2(H18)
IN NITROGEN
WT: 12.53 mg
SCAN RATE: 20.00 deg/min
= BASELINE
ENDO
4.00
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
DATE: 84/12/04

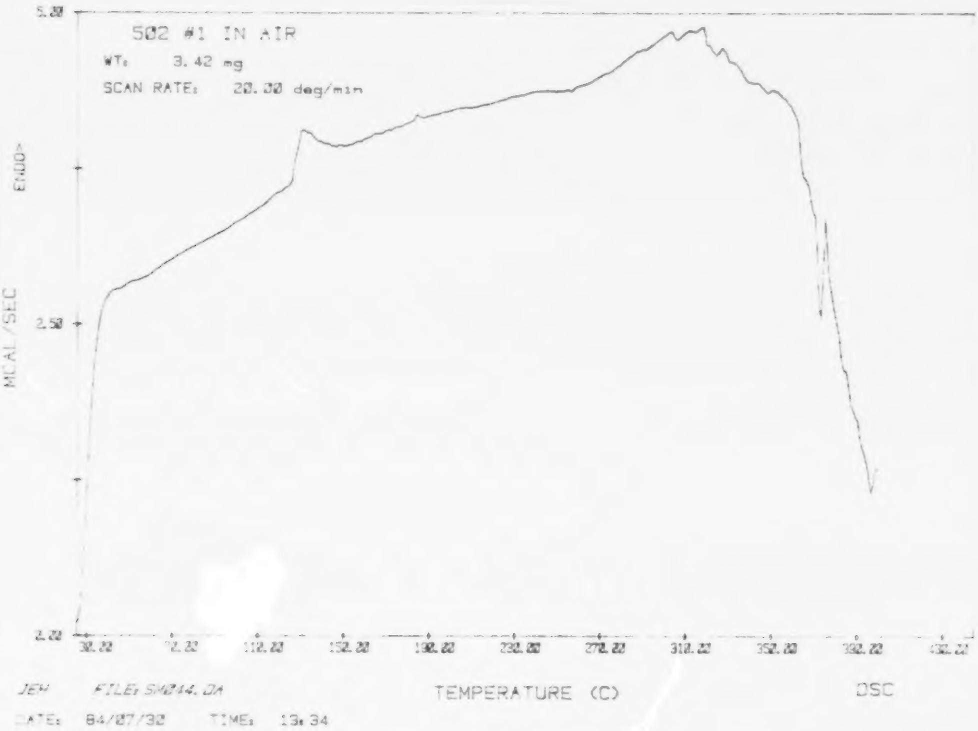
RUN 418

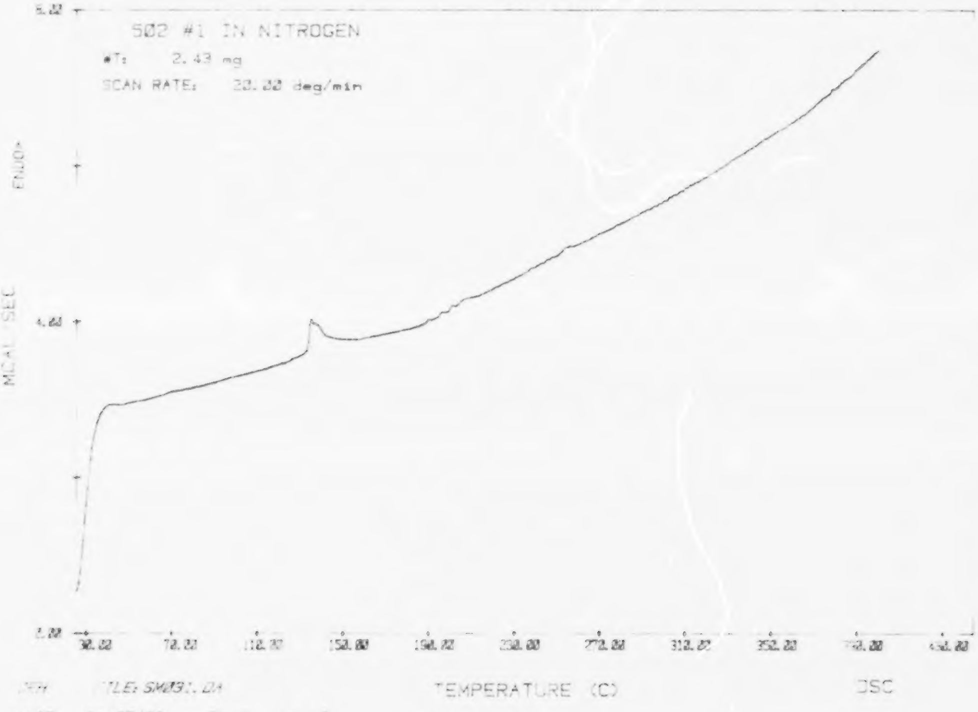




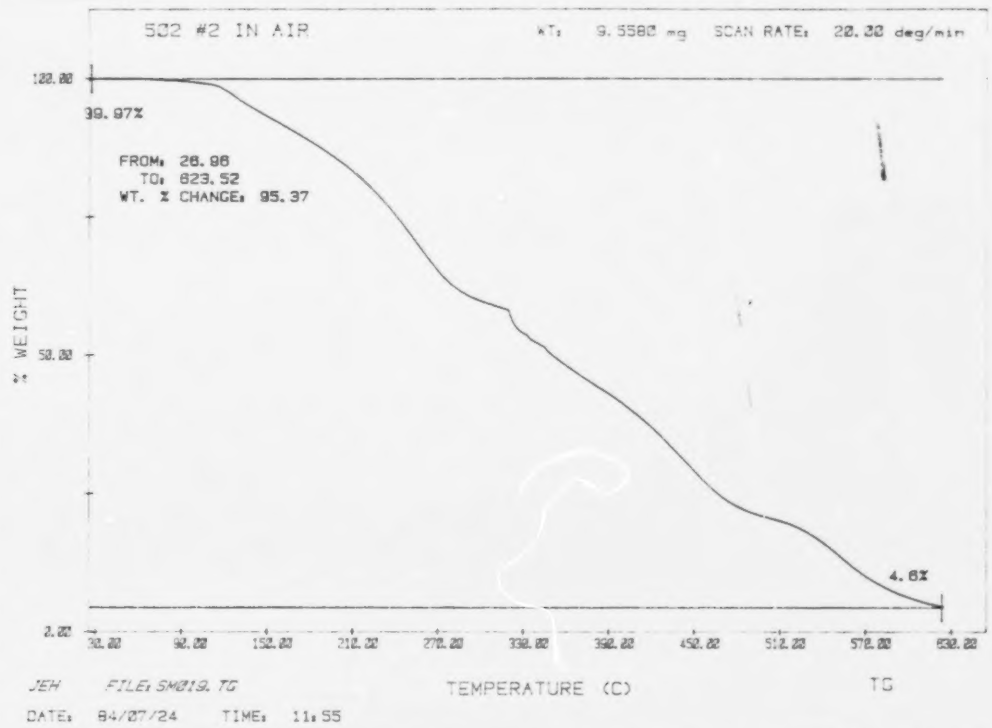
ATE: 84/07/23 TIME: 07:49

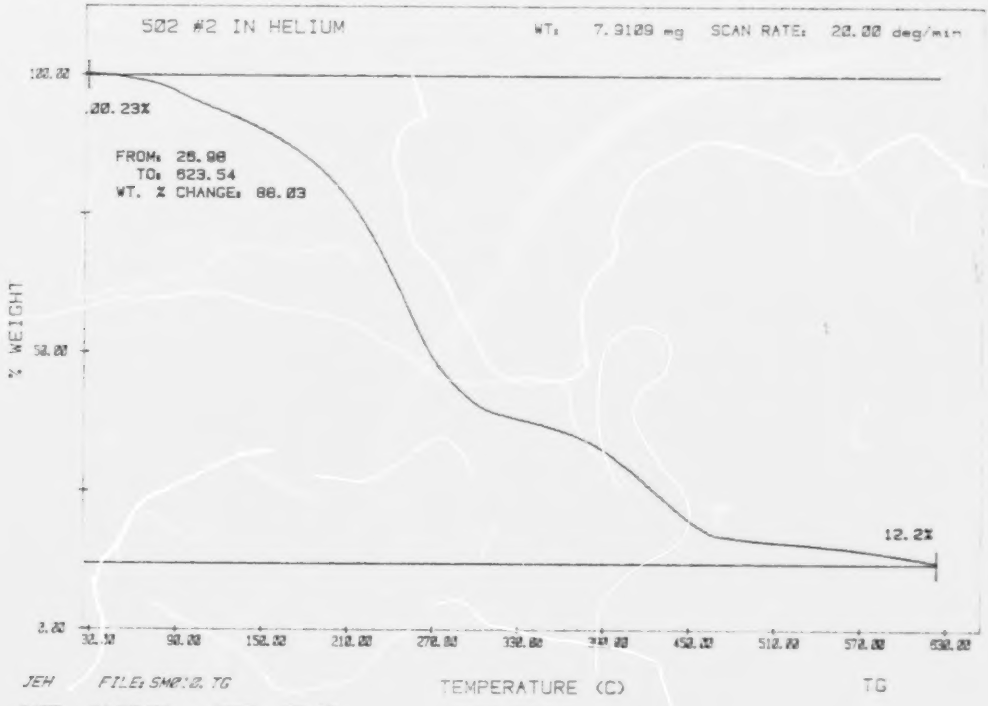
RUN 502


502 #1 IN AIR
WT: 3.42 mg
SCAN RATE: 20.00 deg/min
5.00
2.50
0.00
ENDO>
MCAL/SEC
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
JEH FILE: SM044.DA
DATE: 84/07/30 TIME: 13:34

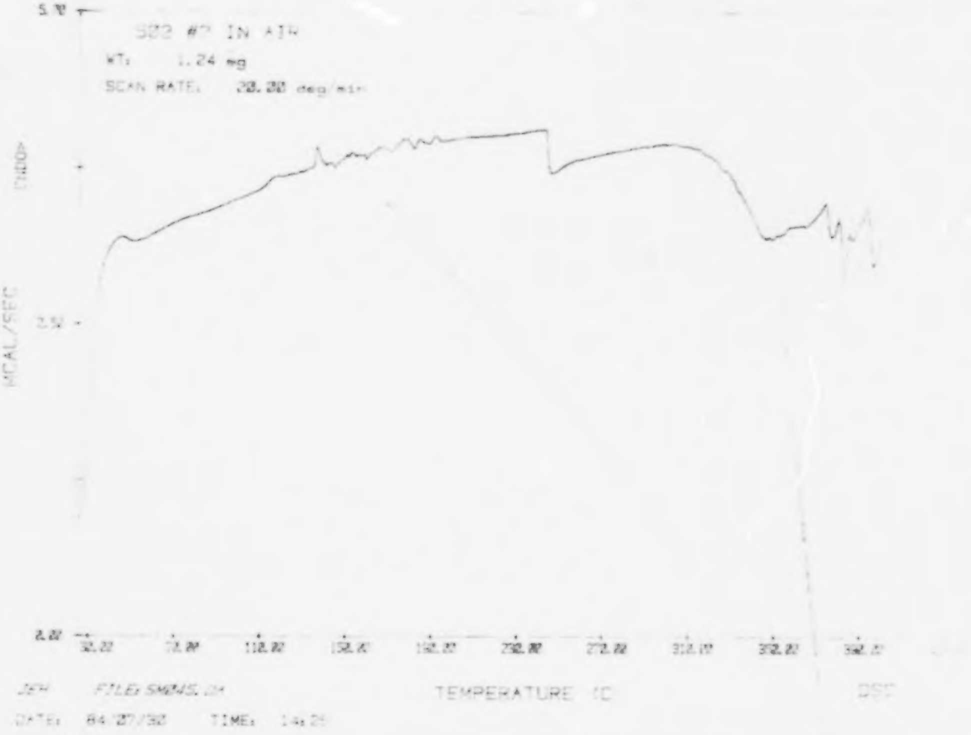

502 #1 IN NITROGEN
WT: 2.43 mg
SCAN RATE: 20.00 deg/min
8.00
4.00
0.00
ENDO>
MCAL/SEC
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
JEH FILE: SM031.DA
DATE: 84/07/26

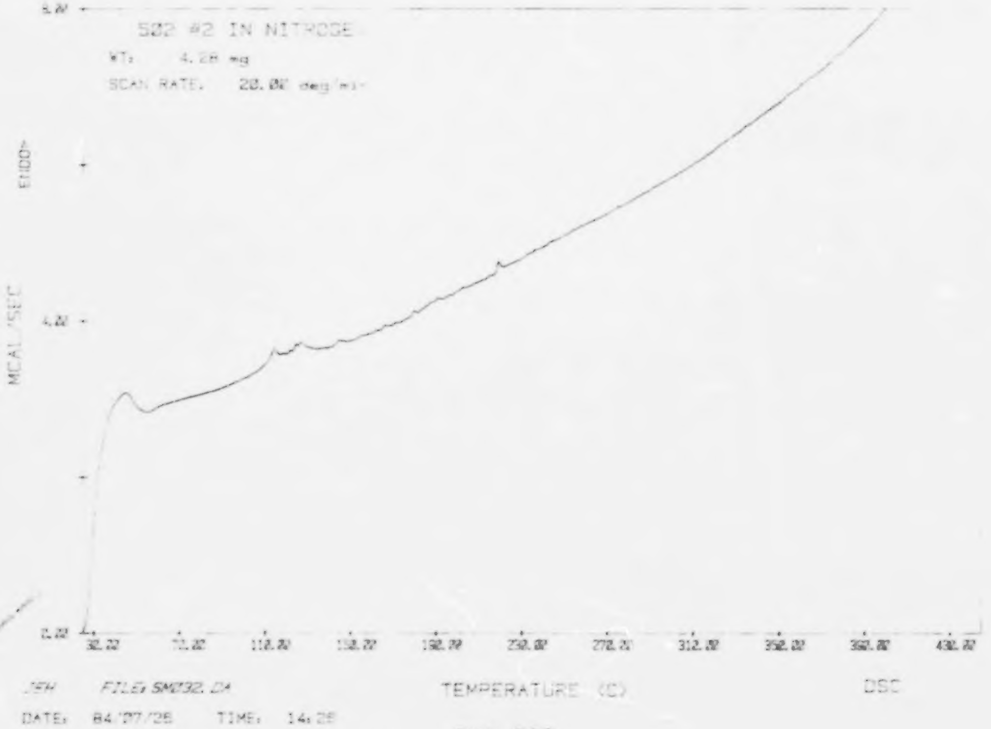
RUN 502


502 #2 IN AIR
WT: 9.5580 mg
SCAN RATE: 20.00 deg/min
100.00
99.97%
FROM: 28.98
TO: 623.52
WT. % CHANGE: 95.37
% WEIGHT
50.00
4.6%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH
FILE: SM019.TG
TEMPERATURE (C)
TG
DATE: 84/07/24
TIME: 11:55

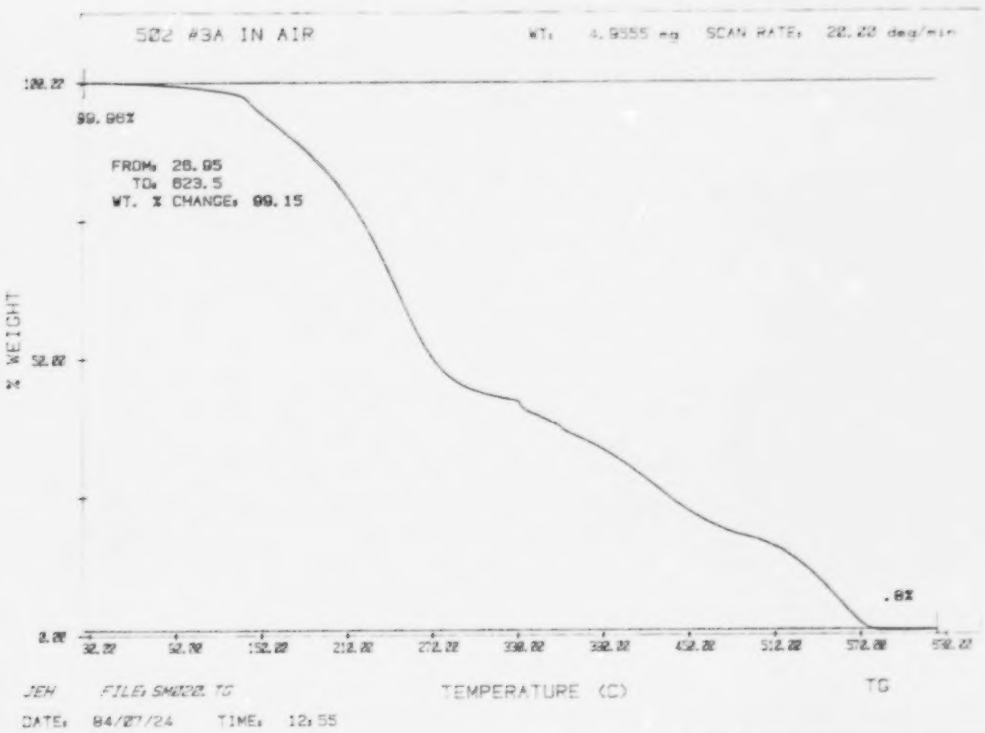

502 #2 IN HELIUM
WT: 7.9109 mg
SCAN RATE: 20.00 deg/min
100.00
100.23%
FROM: 28.98
TO: 623.54
WT. % CHANGE: 88.03
% WEIGHT
50.00
12.2%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH
FILE: SM010.TG
TEMPERATURE (C)
TG
DATE: 84/07/23
TIME: 08:48

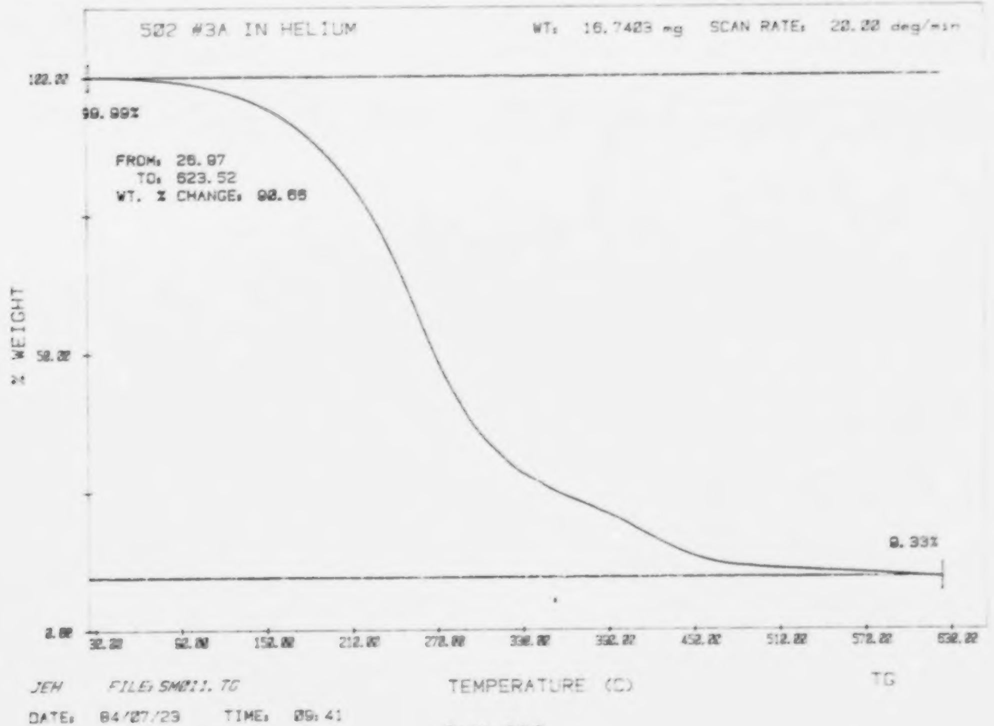
RUN 502


5.00
502 #2 IN AIR
WT: 1.24 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
2.50
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
JEH FILE: SM045.DA
TEMPERATURE (C)
DSC
DATE: 84/07/30 TIME: 14:25

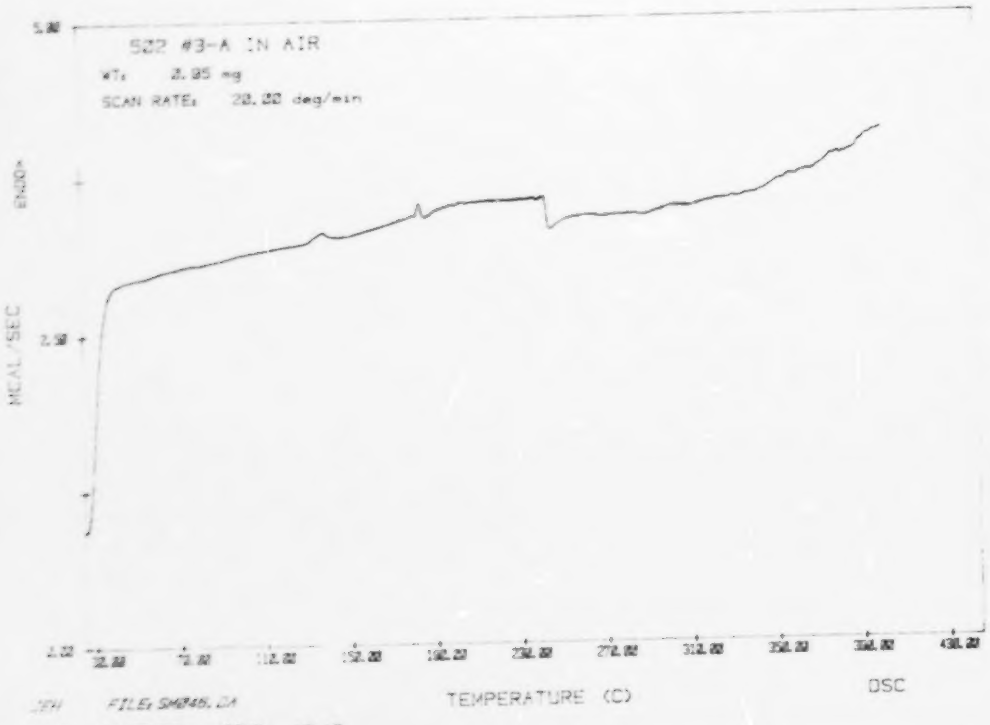

8.00
502 #2 IN NITROGEN
WT: 4.28 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
4.00
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM032.DA
TEMPERATURE (C)
DSC
DATE: 84/07/26 TIME: 14:26

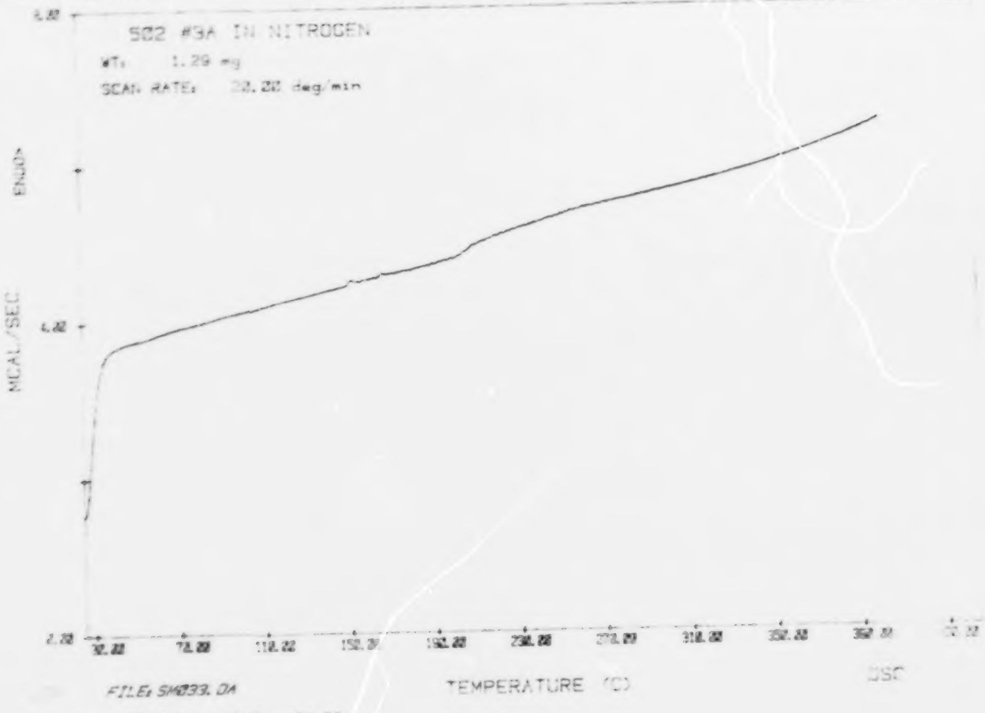
RUN 502


502 #3A IN AIR
WT: 4.9555 mg SCAN RATE: 20.00 deg/min
100.00
99.96%
FROM: 26.95
TO: 623.5
WT. % CHANGE: 99.15
% WEIGHT
50.00
.8%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM020.TG
TEMPERATURE (C)
TG
DATE: 84/07/24 TIME: 12:55

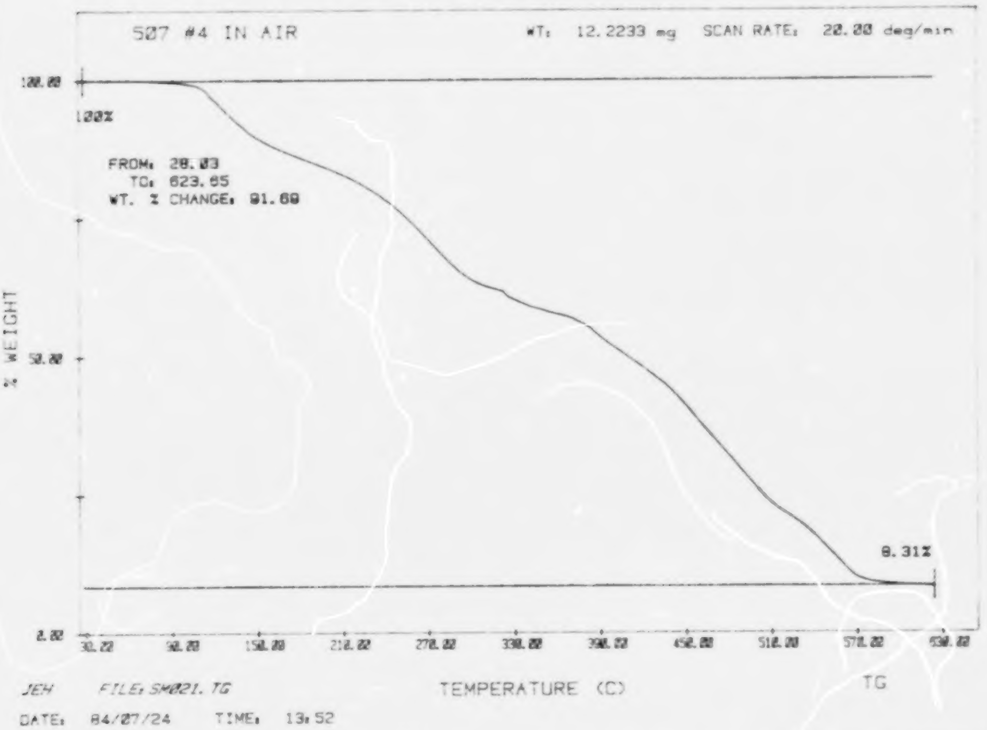

502 #3A IN HELIUM
WT: 16.7403 mg SCAN RATE: 20.00 deg/min
100.00
99.99%
FROM: 26.97
TO: 623.52
WT. % CHANGE: 90.66
% WEIGHT
50.00
9.33%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM011.TG
TEMPERATURE (C)
TG
DATE: 84/07/23 TIME: 09:41

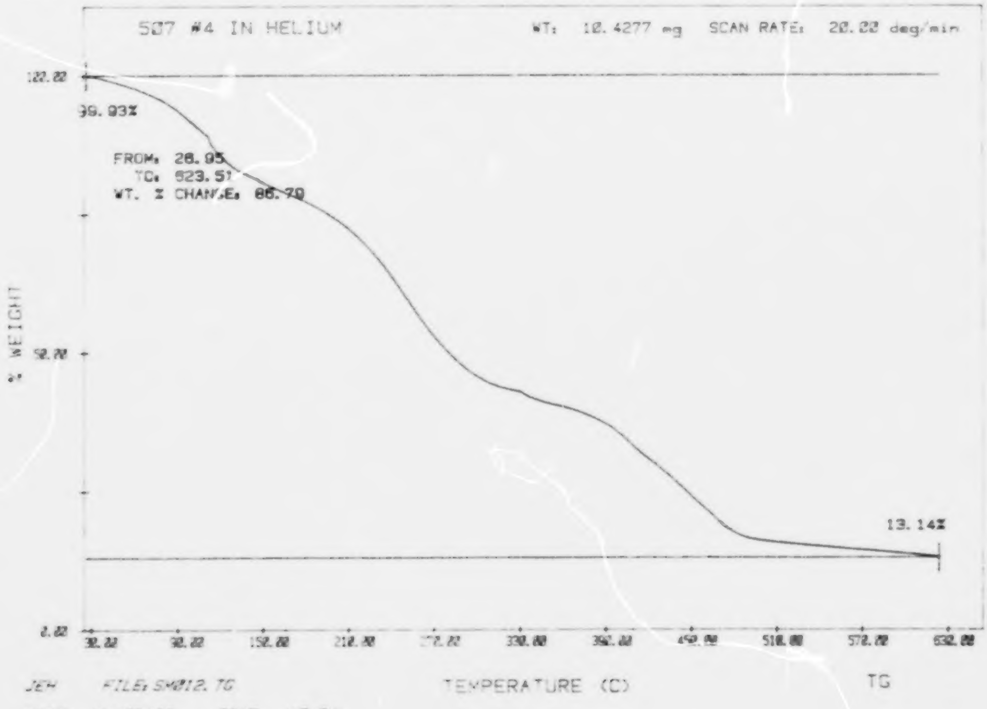
RUN 502


502 #3-A IN AIR
WT: 0.95 mg
SCAN RATE: 20.00 deg/min
5.00
ENDO>
2.50
MCAL/SEC
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
FILE: SM046.DA
DATE: 84/07/30 TIME: 15:13

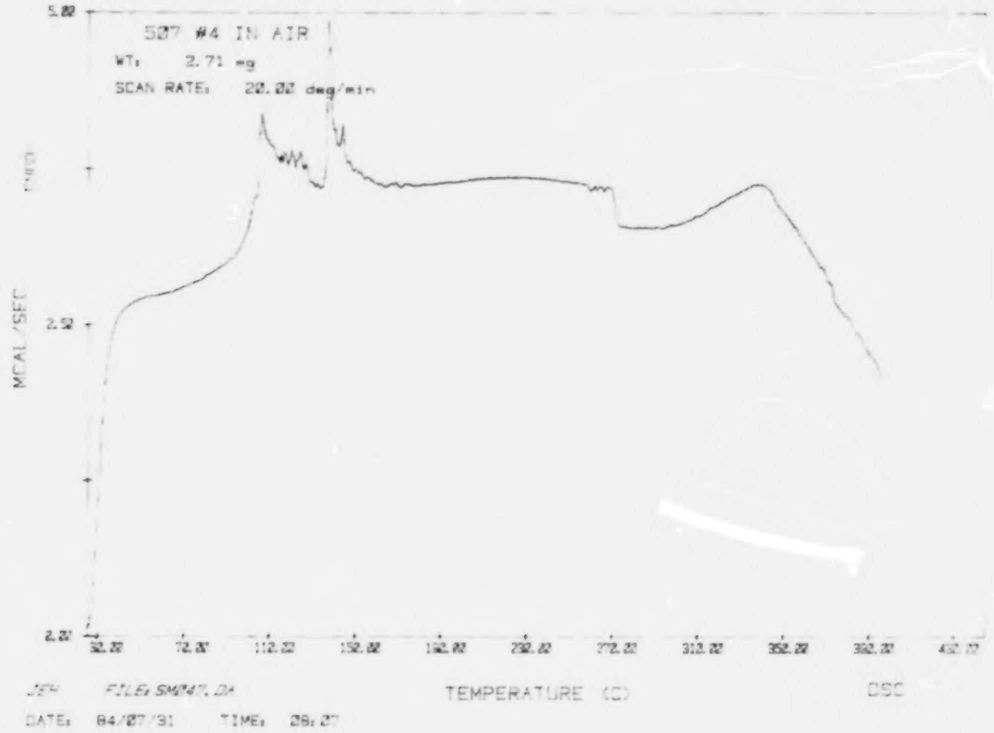

502 #3A IN NITROGEN
WT: 1.29 mg
SCAN RATE: 20.00 deg/min
8.00
ENDO>
4.00
MCAL/SEC
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
TEMPERATURE (C)
DSC
FILE: SM033.DA

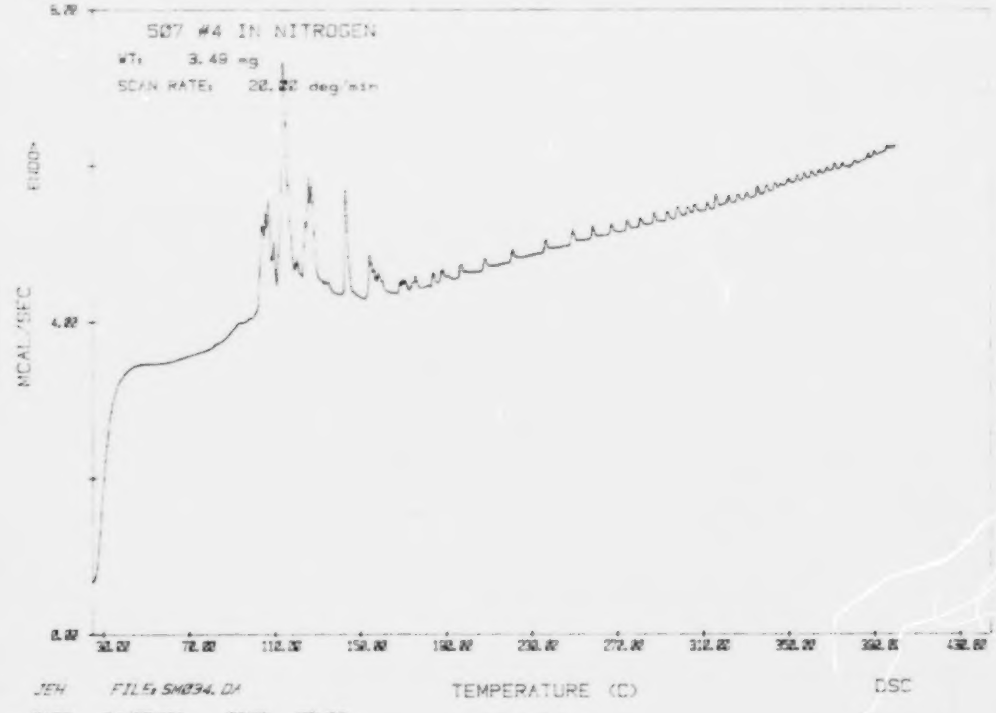
RUN 502


507 #4 IN AIR
WT: 12.2233 mg SCAN RATE: 20.00 deg/min
100.00
100%
FROM: 28.03
TO: 623.65
WT. % CHANGE: 91.68
% WEIGHT
50.00
8.31%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
TEMPERATURE (C)
TG
JEH FILE: SM021. TG
DATE: 84/07/24 TIME: 13:52

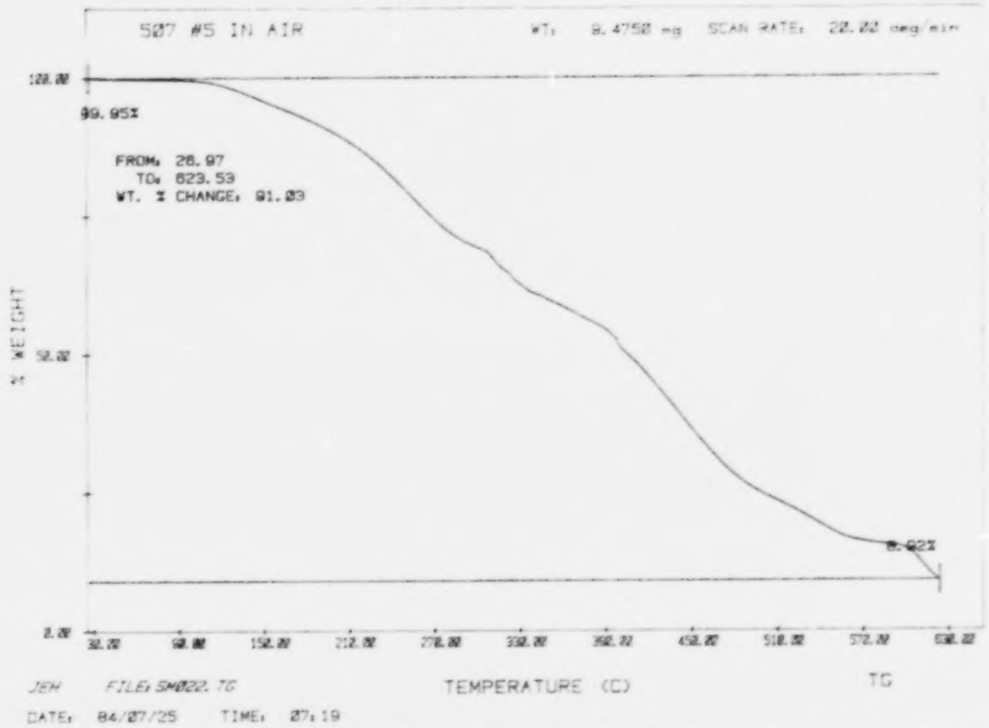

507 #4 IN HELIUM
WT: 10.4277 mg SCAN RATE: 20.00 deg/min
100.00
99.93%
FROM: 28.95
TO: 623.51
WT. % CHANGE: 86.79
% WEIGHT
50.00
13.14%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
TEMPERATURE (C)
TG
JEH FILE: SM012. TG
DATE: 84/07/23 TIME: 10:34

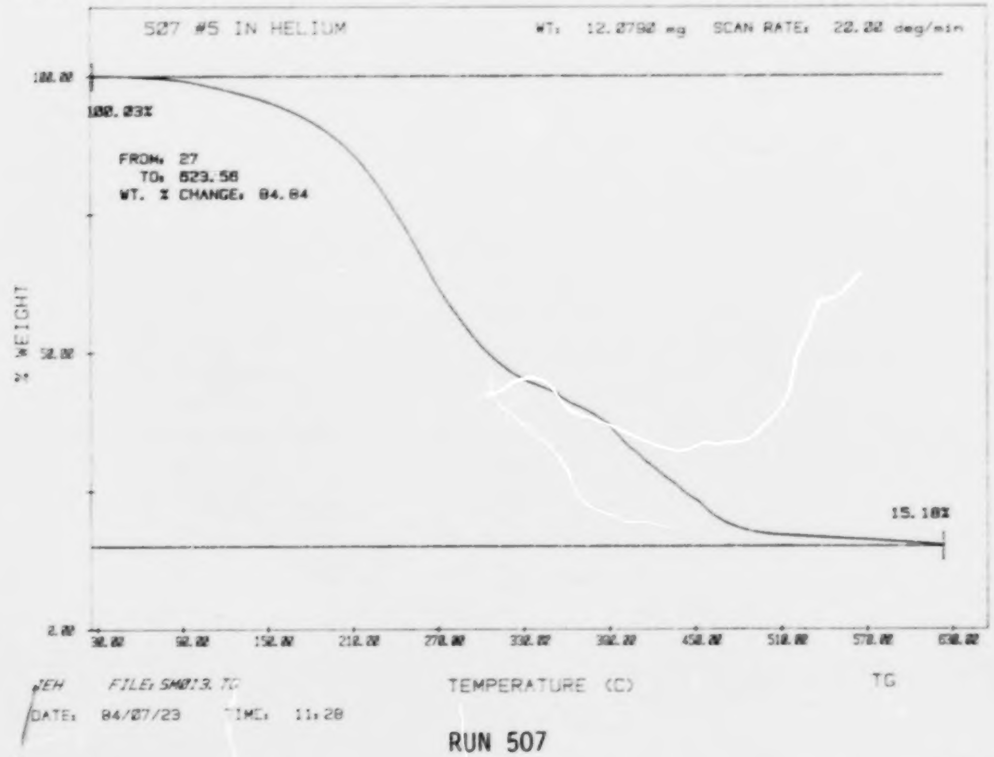
RUN 507


507 #4 IN AIR
WT: 2.71 mg
SCAN RATE: 20.00 deg/min
ENDO
MCAL/SEC
5.00
2.50
0.00
32.00
72.00
112.00
152.00
192.00
232.00
272.00
312.00
352.00
392.00
432.00
JEH FILE: SM047.DA
TEMPERATURE (C)
DSC
DATE: 84/07/31 TIME: 08:27

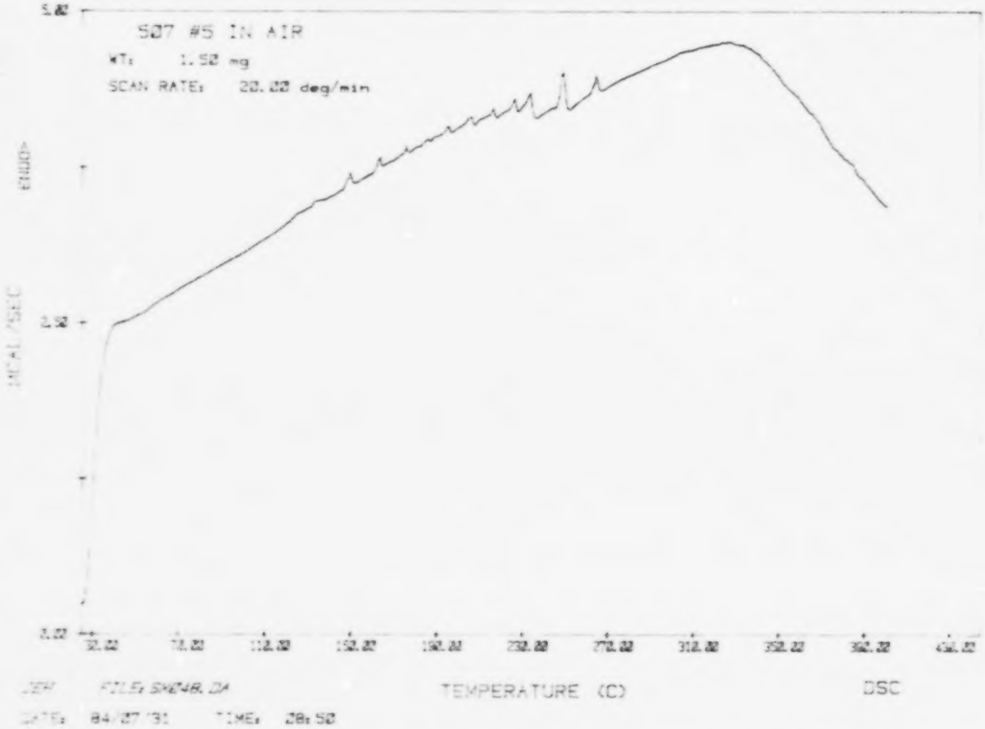

507 #4 IN NITROGEN
WT: 3.49 mg
SCAN RATE: 20.00 deg/min
ENDO
MCAL/SEC
8.00
4.00
0.00
30.00
72.00
112.00
150.00
192.00
230.00
272.00
312.00
352.00
392.00
432.00
JEH FILE: SM034.DA
TEMPERATURE (C)
DSC
DATE: 84/07/27 TIME: 09:27

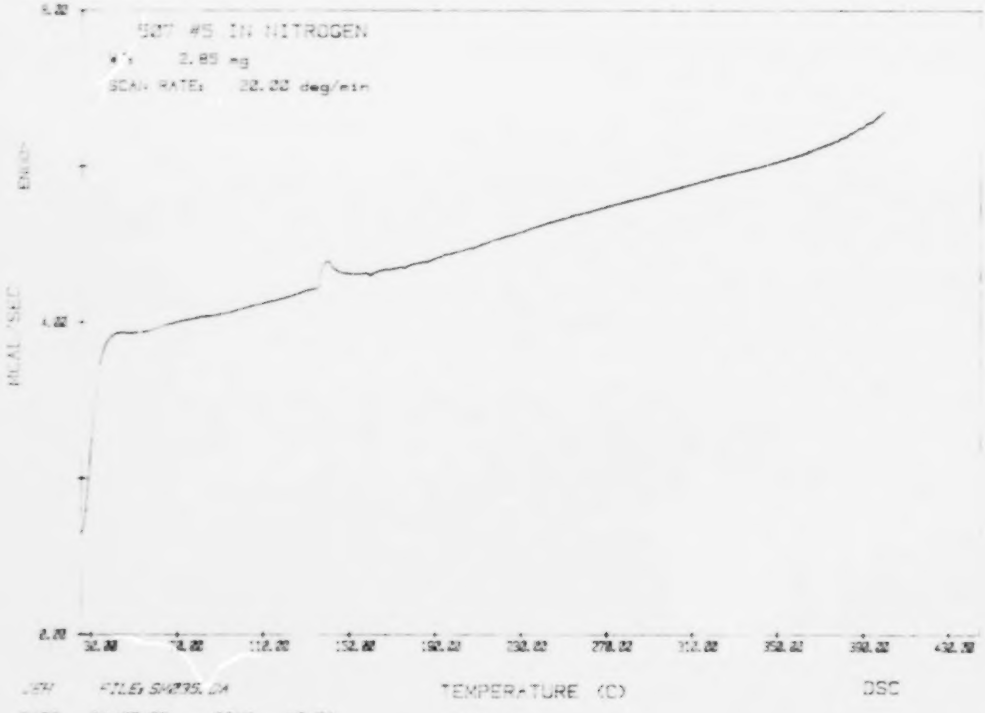
RUN 507


507 #5 IN AIR
WT: 8.4750 mg SCAN RATE: 20.00 deg/min
100.00
99.95%
FROM: 28.97
TO: 623.53
WT. % CHANGE: 91.03
% WEIGHT
50.00
8.92%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM022.TG
TEMPERATURE (C)
TG
DATE: 84/07/25 TIME: 07:19

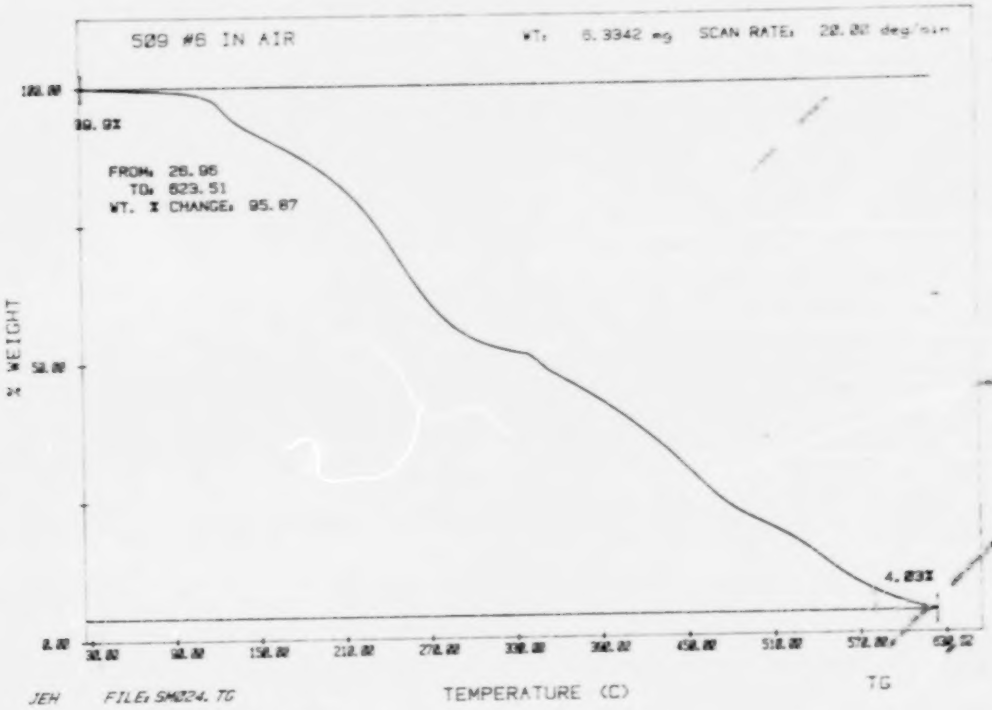

507 #5 IN HELIUM
WT: 12.0790 mg SCAN RATE: 20.00 deg/min
100.00
100.03%
FROM: 27
TO: 623.58
WT. % CHANGE: 84.84
% WEIGHT
50.00
15.18%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM013.TG
TEMPERATURE (C)
TG
DATE: 84/07/23 TIME: 11:28

RUN 507


507 #5 IN AIR
WT: 1.50 mg
SCAN RATE: 20.00 deg/min
5.00
2.50
0.00
ENDO>
MCAL/SEC
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM048.DA
TEMPERATURE (C)
DSC
DATE: 84/07/31 TIME: 20:50

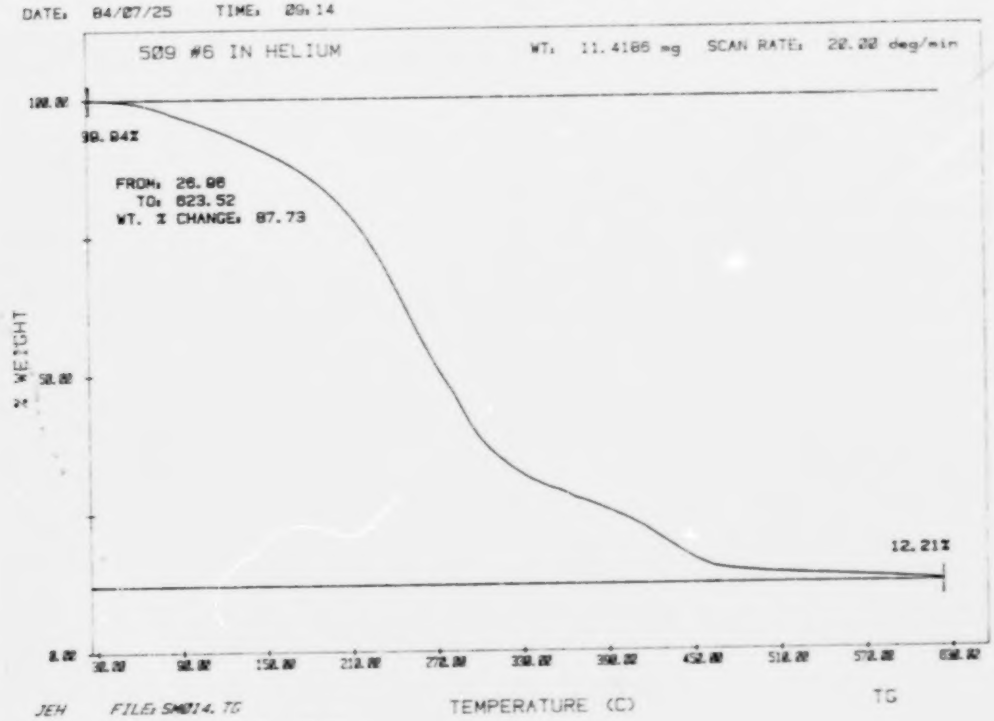

507 #5 IN NITROGEN
WT: 2.85 mg
SCAN RATE: 20.00 deg/min
8.00
4.00
0.00
ENDO>
MCAL/SEC
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM035.DA
TEMPERATURE (C)
DSC
DATE: 84/07/27 TIME: 10:50

RUN 507



JEH *FILE: SM024. TG*

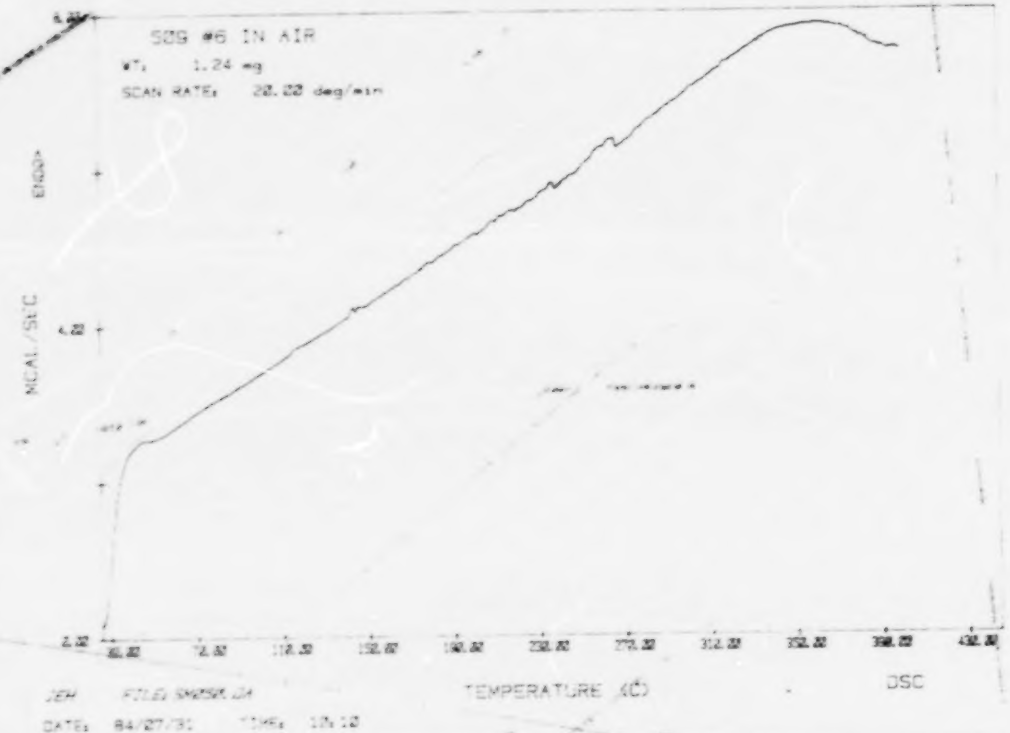
DATE: 84/07/25 TIME: 09:14

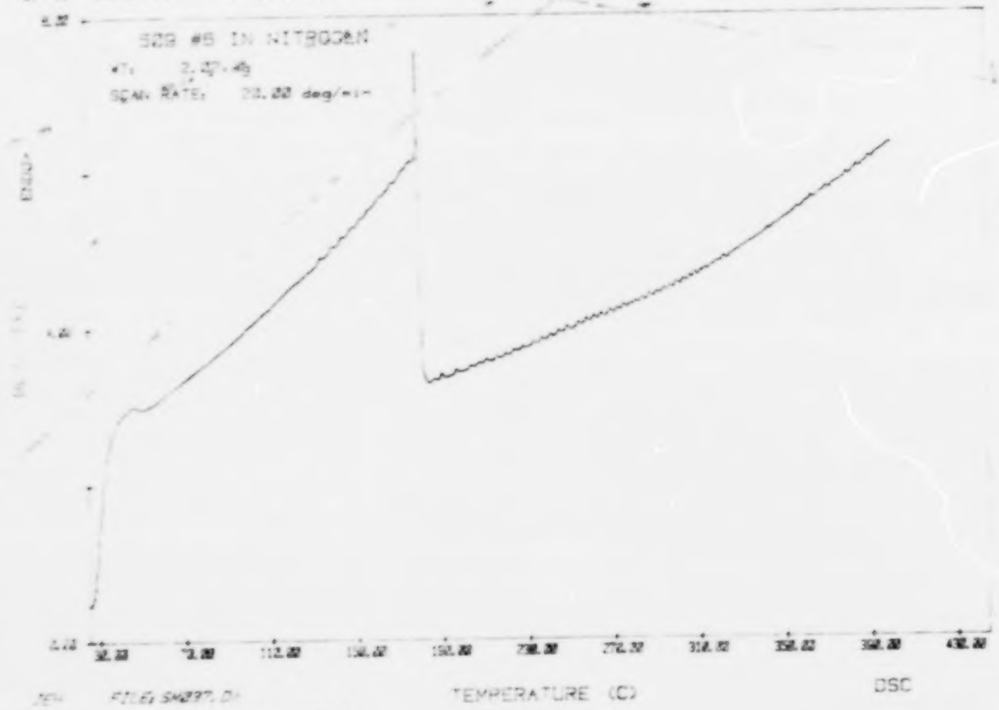


JEH *FILE: SM014. TG*

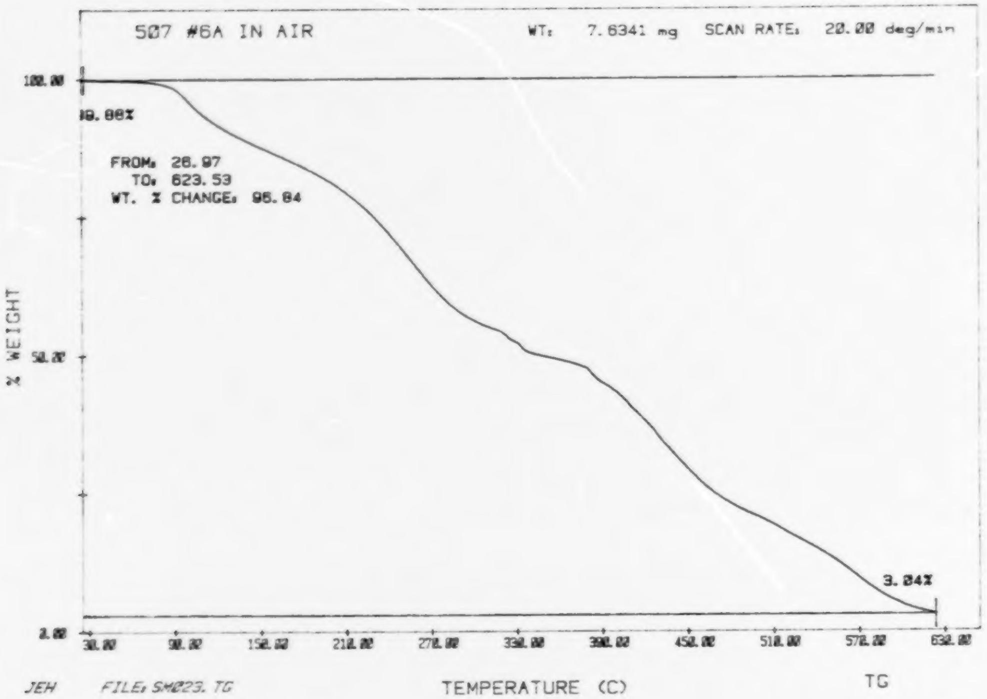
DATE: 84/07/23 TIME: 12:58

RUN 509


509 #6 IN AIR
WT: 1.24 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
8.00
4.00
0.00
32.00
72.00
112.00
152.00
192.00
232.00
272.00
312.00
352.00
392.00
432.00
TEMPERATURE (C)
DSC
JEH FILE: SM0509.DA
DATE: 84/07/31 TIME: 10:10

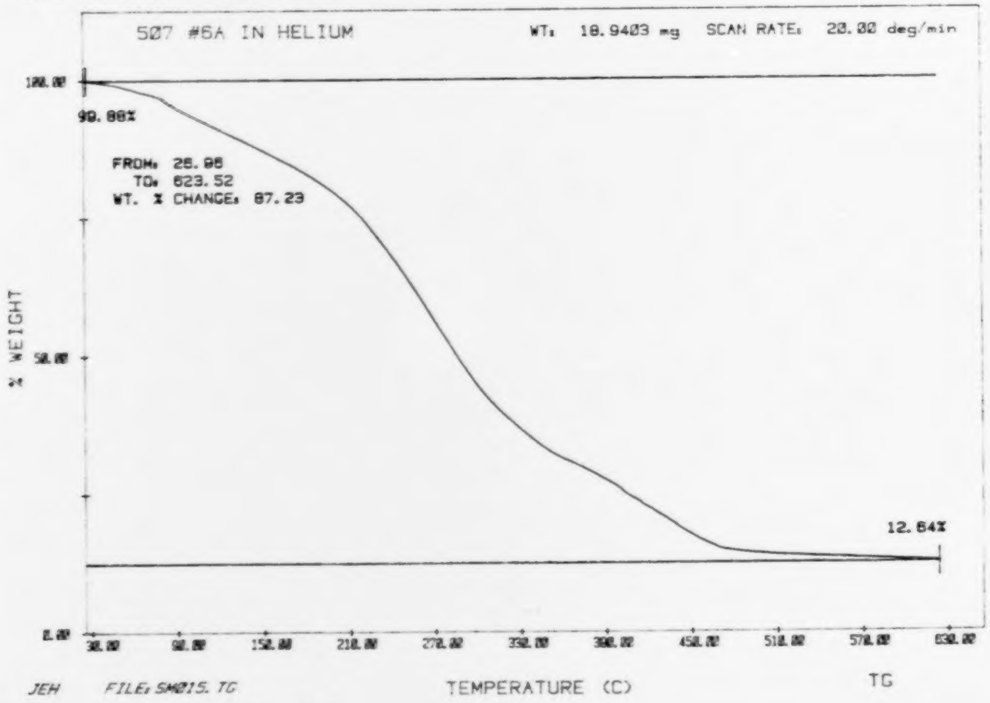

509 #6 IN NITROGEN
WT: 2.07 mg
SCAN RATE: 20.00 deg/min
ENDO>
8.00
4.00
0.00
32.00
72.00
112.00
152.00
192.00
232.00
272.00
312.00
352.00
392.00
432.00
TEMPERATURE (C)
DSC
JEH FILE: SM0507.D1
DATE: 84/07/27 TIME: 13:05

RUN 509



JEH FILE: SM023. TG

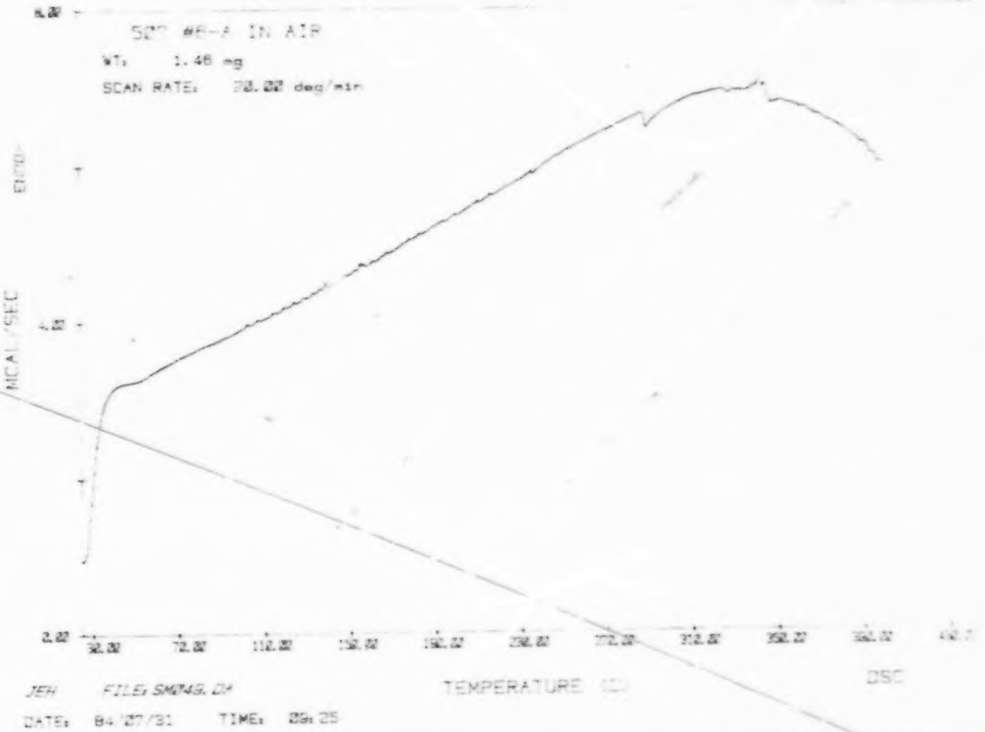
DATE: 84/07/25 TIME: 08:13

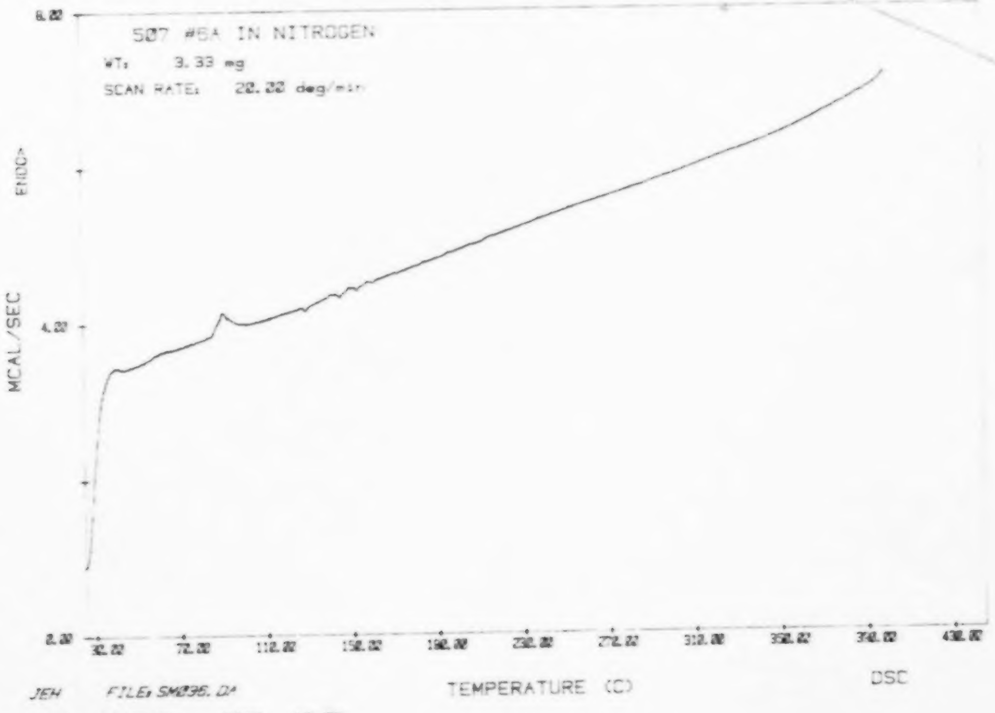


JEH FILE: SM015. TG

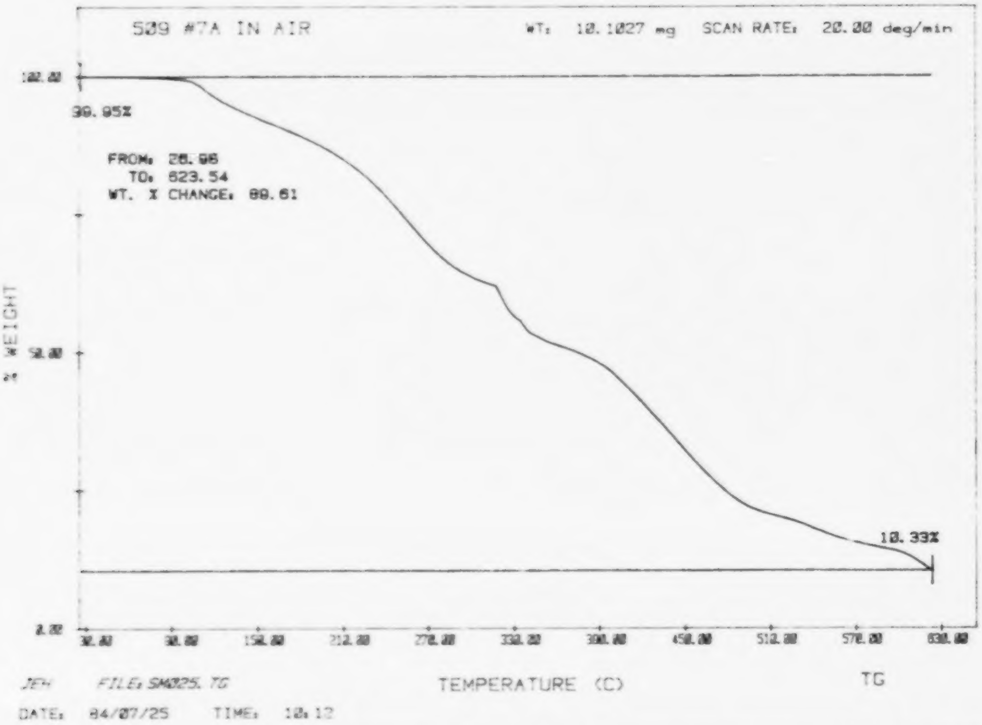
DATE: 84/07/23 TIME: 13:52

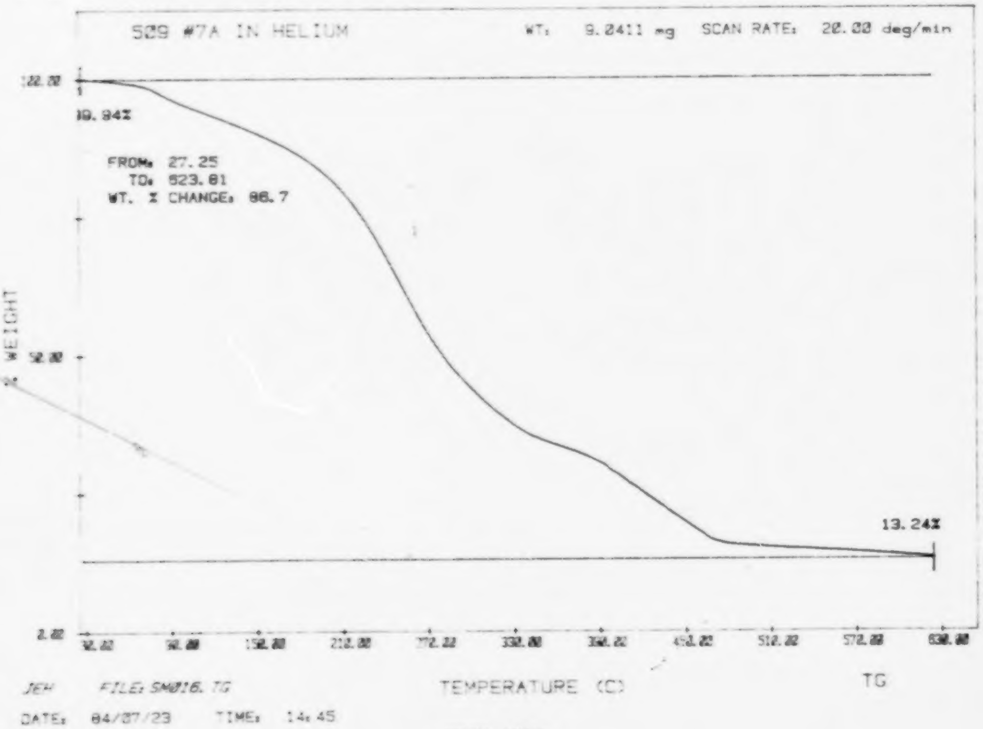
RUN 507


8.00
507 #6-A IN AIR
WT: 1.48 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
4.00
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.0
TEMPERATURE (C)
DSC
JEH FILE: SM049.DA
DATE: 84/07/31 TIME: 09:25

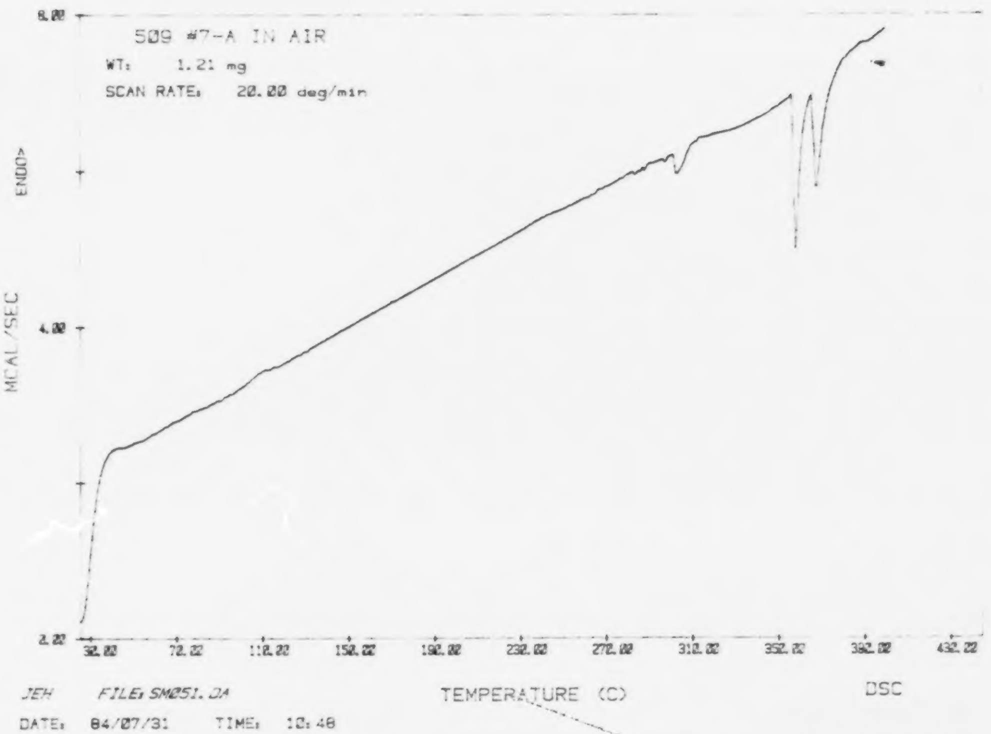

8.00
507 #6A IN NITROGEN
WT: 3.33 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
4.00
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
TEMPERATURE (C)
DSC
JEH FILE: SM036.DA
DATE: 84/07/27 TIME: 12:07

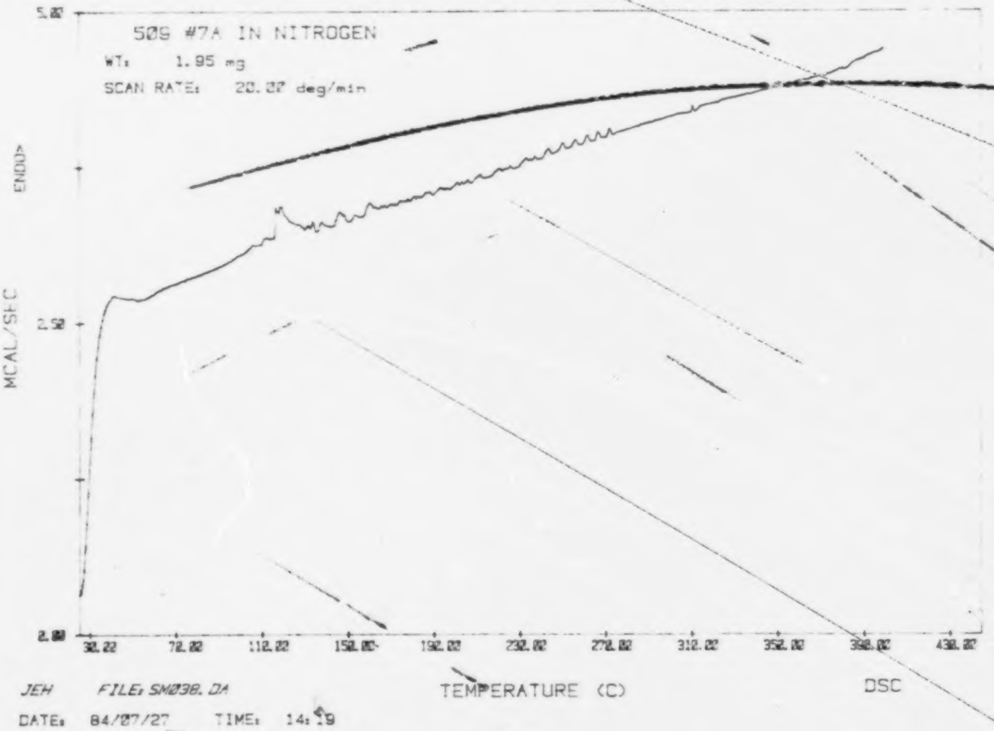
RUN 507


509 #7A IN AIR
WT: 10.1027 mg
SCAN RATE: 20.00 deg/min
100.00
99.95%
FROM: 28.96
TO: 623.54
WT. % CHANGE: 89.61
% WEIGHT
50.00
10.33%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH
FILE: SM025.TG
TEMPERATURE (C)
TG
DATE: 84/07/25
TIME: 10:12

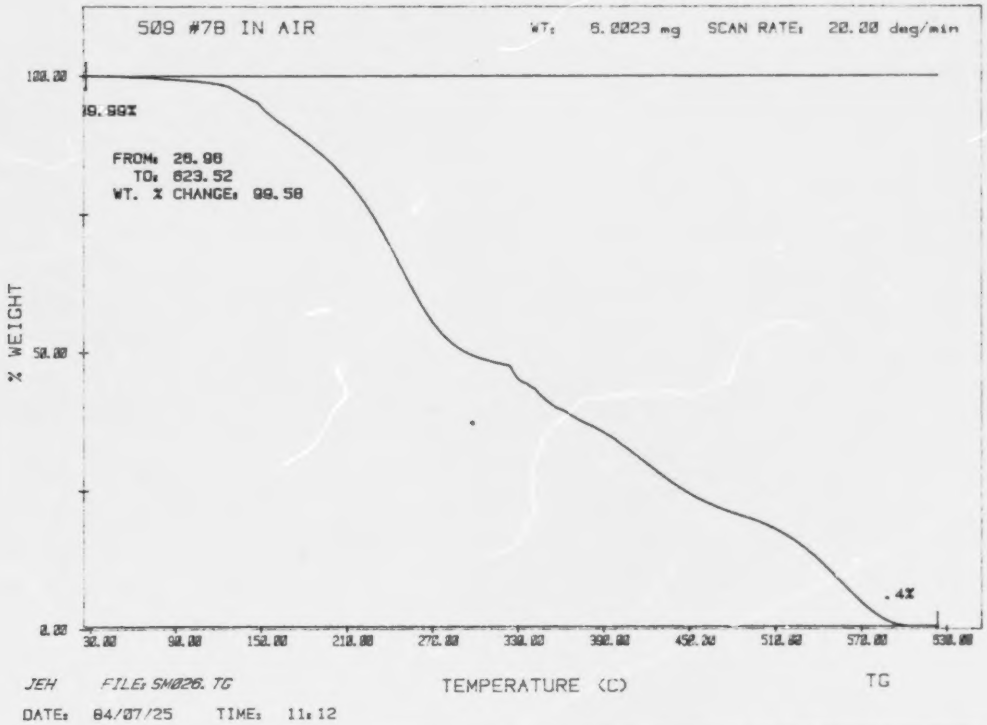

509 #7A IN HELIUM
WT: 9.0411 mg
SCAN RATE: 20.00 deg/min
100.00
99.84%
FROM: 27.25
TO: 623.81
WT. % CHANGE: 86.7
% WEIGHT
50.00
13.24%
0.00
30.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH
FILE: SM016.TG
TEMPERATURE (C)
TG
DATE: 84/07/23
TIME: 14:45

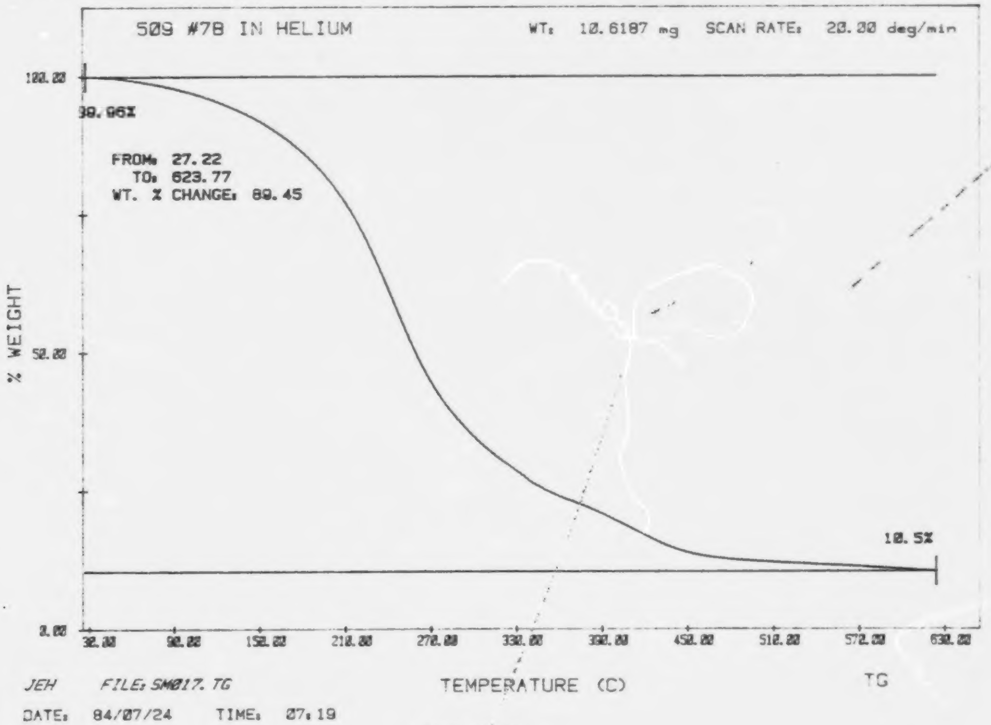
RUN 509


509 #7-A IN AIR
WT: 1.21 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
6.00
4.00
2.00
32.00
72.00
112.00
152.00
192.00
232.00
272.00
312.00
352.00
392.00
432.00
JEH FILE: SM051.DA
TEMPERATURE (C)
DSC
DATE: 84/07/31 TIME: 10:48

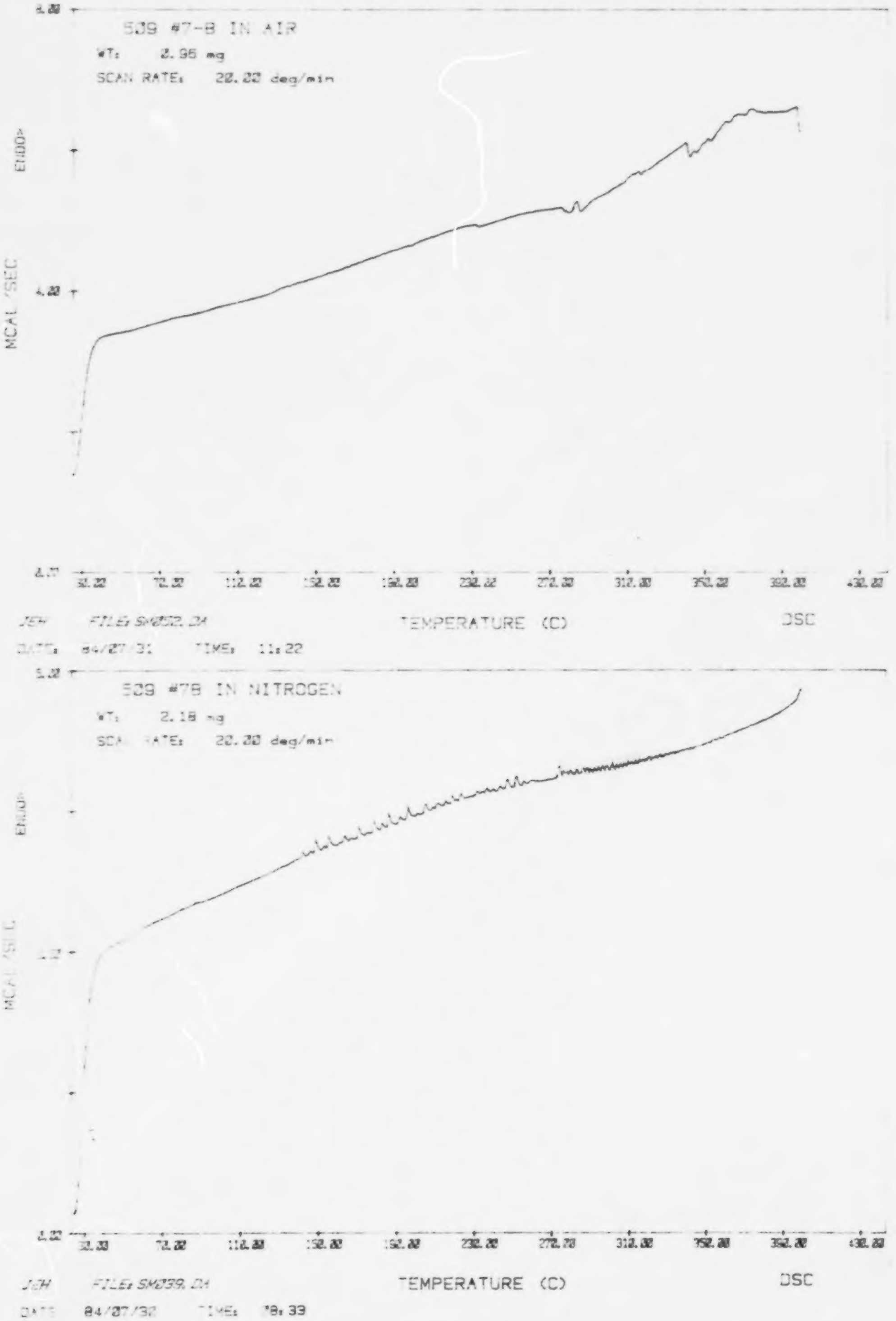

509 #7A IN NITROGEN
WT: 1.95 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
5.00
2.50
0.00
32.00
72.00
112.00
152.00
192.00
232.00
272.00
312.00
352.00
392.00
432.00
JEH FILE: SM038.DA
TEMPERATURE (C)
DSC
DATE: 84/07/27 TIME: 14:19

RUN 509


509 #7B IN AIR
WT: 6.0023 mg SCAN RATE: 20.00 deg/min
100.00
99.99%
FROM: 28.98
TO: 623.52
WT. % CHANGE: 99.58
% WEIGHT
50.00
.4%
0.00
32.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM026.TG
TEMPERATURE (C)
TG
DATE: 84/07/25 TIME: 11:12


509 #7B IN HELIUM
WT: 10.6187 mg SCAN RATE: 20.00 deg/min
100.00
99.96%
FROM: 27.22
TO: 623.77
WT. % CHANGE: 89.45
% WEIGHT
50.00
10.5%
0.00
32.00
90.00
150.00
210.00
270.00
330.00
390.00
450.00
510.00
570.00
630.00
JEH FILE: SM017.TG
TEMPERATURE (C)
TG
DATE: 84/07/24 TIME: 07:19

RUN 509


8.00
509 #7-B IN AIR
WT: 0.95 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
4.00
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM052.DA
TEMPERATURE (C)
DSC
DATE: 84/07/31 TIME: 11:22
5.00
509 #7B IN NITROGEN
WT: 2.18 mg
SCAN RATE: 20.00 deg/min
ENDO>
MCAL/SEC
0.00
30.00
70.00
110.00
150.00
190.00
230.00
270.00
310.00
350.00
390.00
430.00
JEH FILE: SM039.DA
TEMPERATURE (C)
DSC
DATE 84/07/30 TIME: 08:33

RUN 509